PB84-169994

# EPA (Environmental Protection Agency) Method Study 23A, Method 501.1 Trihalomethanes by Purge and Trap

Monsanto Research Corp., Dayton, OH

Prepared for

Environmental Monitoring and Support Lab.
Cincinnati, OH

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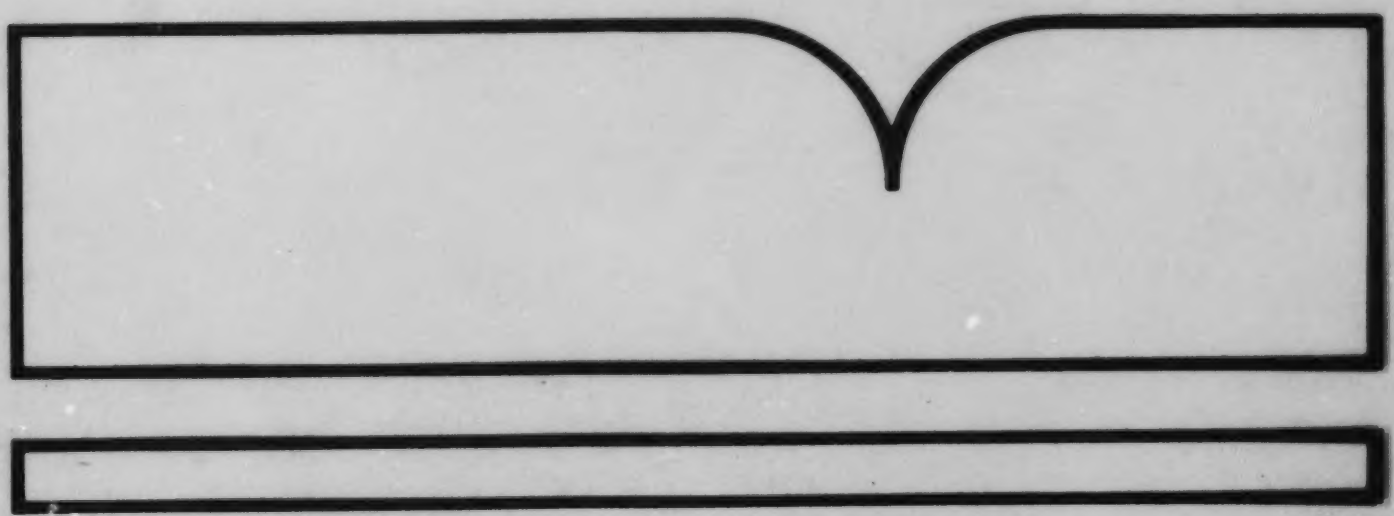

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-169994

EPA-600/4-84-020
March 1984

# EPA METHOD STUDY 23A, METHOD 501.1, TRIHALOMETHANES BY PURGE AND TRAP

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**TECHNICAL REPORT DATA**
*(Please read Instructions on the reverse before completing)*

| | |
|---|---|
| 1. REPORT NO. EPA-600/4-84-020 | 2. |
| 3. RECIPIENT'S ACCESSION NO. PB84-169994 | |
| 4. TITLE AND SUBTITLE EPA METHOD STUDY 23A, METHOD 501.1, TRIHALOMETHANES BY PURGE AND TRAP | 5. REPORT DATE March 1984 |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) B.J. Warner, S.C. Cheng, C.S. Friedman, S. Mitrosky, A.D. Snyder, and C.R. McMillin | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Monsanto Research Corporation Dayton, OH 45407 | 10. PROGRAM ELEMENT NO. |
| | 11. CONTRACT/GRANT NO. 68-03-2856 |
| 12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring and Support Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268 | 13. TYPE OF REPORT AND PERIOD COVERED |
| | 14. SPONSORING AGENCY CODE EPA/600/06 |
| 15. SUPPLEMENTARY NOTES | |

16. ABSTRACT

The experimental design and results of a validation study for an analytical method to detect trihalomethanes in water are described herein. This method consisted of a liquid/liquid extraction using pentane and subsequent direct analysis by gas chromatography using an electron capture detector. The six concentrations of spiking solutions contained chloroform, bromodichloromethane, chlorodibromomethane and bromoform. The two waters used in the study were distilled and drinking water, both supplied by the individual laboratories. Statistical analyses and conclusions in this report are based on analytical data obtained by twenty collaborating laboratories. This report was submitted in partial fulfillment of contract 68-03-2856 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. The report covers a period from September 1979 to December 1982.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| | | |

| | | |
|---|---|---|
| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES 116 |
| | 20. SECURITY CLASS *(This page)* | 22. PRICE |

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the hard work and cooperation of the staff of the Quality Assurance Branch, EMSL, who assisted in the study. They especially acknowledge the excellent technical assistance, guidance, and understanding of Raymond Wesselman of EMSL. Also acknowledged is the work of Dr. Thomas Bishop at Battelle Memorial Laboratories, Columbus, Ohio, for statistical analysis of the data under Contract No. 68-03-2624.

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This report was submitted in fulfillment of contract 68-03-2856 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 1979 to December 1982.

## ABSTRACT

The experimental design and the results of a interlaboratory study for an analytical method to detect trihalomethanes in water are described herein. In EPA Method 501.1, trihalomethanes are extracted by an inert gas which is bubbled through the aqueous sample. The vapors are then trapped on a short column containing a suitable sorbent. The trapped compounds are subsequently thermally desorbed onto the head of a gas chromatographic column. An electrolytic conductivity detector is used to measure the compounds. The spiking solutions contained chloroform, bromodichloromethane, chlorodibromomethane, and bromoform at six concentrations. Two water types, distilled and drinking water, were supplied by the individual analytical laboratories. Statistical analyses and conclusions are based on analytical data obtained by twenty collaborating laboratories.

Participating laboratories were selected based upon technical evaluation of proposals and upon the analyses results of prestudy samples. The data obtained from the interlaboratory study were analyzed employing a series of computer programs known as the Interlaboratory Method Validation Study (IMVS) system which was designed to implement ASTM procedure D2777. The statistical analyses included tests for the rejection of outliers, estimation of mean recovery (accuracy), estimation of single-analyst and overall precision, and tests for the effects of water type on accuracy and prevision.

Federal agencies, states, municipalities, universities, private laboratories, and industry should find this interlaboratory study useful in monitoring and controlling pollution in the environment.

Robert L. Booth, Director

## FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL)-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water.
- Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This publication, Interlaboratory Study 23A, Method 501.1, Determination of Trihalomethanes by Purge and Trap, reports the results of EPA's interlaboratory method study for the trihalomethanes: chloroform, bromodichloromethane, chlorodibromomethane, and bromoform.



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## SECTION 1

## INTRODUCTION

The various analytical laboratories of the U.S. Environmental Protection Agency (EPA) gather water quality data to provide information on water resources, to assist research activities, and to evaluate pollution abatement activities. The success of these pollution control activities depends upon the reliability of the data provided by the laboratories, particularly when legal action is involved.

The Environmental Monitoring and Support Laboratory-Cincinnati (EMSL-Ci), of the EPA develops analytical methods and conducts quality assurance programs for the water laboratories. The quality assurance program of EMSL is designed to maximize the reliability and legal defensibility of all water quality information collected by EPA laboratories. The responsibility for these activities of EMSL is assigned to the Quality Assurance Branch (QAB). One of these activities is to conduct interlaboratory tests of the methods. This study reports the results of the validation effort on Method 501.1 (Study 23A).

The method evaluated in this report was prepared by the EMSL-Cincinnati staff at the request of the Office of Drinking Water, with cooperation from the Technical Support Division, Office of Drinking Water and the Municipal Environmental Research Laboratory. Additional comments and suggestions from the Health Effects Research Laboratory are gratefully acknowledged.

The interlaboratory study of EPA Method 501.1 consisted of three distinct phases. Phase I involved the analysis of the prestudy

samples by 20 participating laboratories. Two samples were analyzed for each of the four trihalomethanes, one in organic-free water and one in drinking water. Both waters were supplied by the individual participating laboratories. The objective of Phase I was to become familiar with the methodology employed and to identify any potential problems associated with the analytical methodology. Accuracy was not as important as being familiar with the methodology. A short report, including the data obtained and any potential problems encountered, was received at the completion of Phase I from each subcontracting laboratory.

Phase II consisted of a prestudy conference held at U.S. Environmental Protection Agency (EPA), Cincinnati, Ohio. Each subcontracting laboratory sent at least one participant to the meeting. The analyst, or principal analyst if more than one analyst was involved, attended this meeting. This meeting, which was held after the data from the prestudy had been evaluated, was designed to examine the results of the prestudy and to discuss any problems encountered in the methodology.

Phase III of the interlaboratory study required the analysis of the study samples. In the case of Method 501.1, the analysis of the four trihalomethanes in both distilled water and drinking water was required at each of six concentrations (three Youden pairs). Again, the participating laboratories supplied the required water samples for these analyses. In addition, the participating laboratories analyzed their distilled and tap water blanks. Each participating laboratory then issued a report containing all data obtained, copies of all chromatograms, and any comments.

The final step in the study was to conduct a statistical analysis of all data obtained. This analysis was conducted by Battelle Memorial Laboratories, Columbus, Ohio, under contract with the U.S. EPA.

## SECTION 2

## CONCLUSIONS

The objective of this interlaboratory study was to characterize the performance of Method 501.1 in terms of accuracy, overall precision, single-analyst precision, and the effect of water type on accuracy and precision. Through statistical analyses of 960 analyzed values, estimates of accuracy and precision were made and expressed as regression equations, shown in Table 1. The slope of the regression equations, expressed as percentages, are given in Table 2.

The accuracy is obtained by comparing the mean recovery to the true values of the concentrations. The accuracy, expressed as percent recovery, ranges from 92% to 108% in both water type. The accuracy of the method based on percent recovery is excellent. A slight high bias is seen in the tap water but it is not statistically significant. The probable cause of this slight bias is background in the tap water.

The overall standard deviation of the analytical results is an indication of the precision associated with the measurement generated by a group of laboratories. The percent relative standard deviation (% RSD), ranges from 18% to 32%. The overall standard deviation is considered to be good. Over the range of 0.8 µg/L to 550 µg/L, the best precision occurs at the middle Youden pair which is near the drinking water standards.

The single-analyst standard deviation indicates the precision associated within a single laboratory. The percent relative

TABLE 1. REGRESSION EQUATIONS FOR ACCURACY AND PRECISION FOR COMPOUNDS 1 - 4

| Water type | Chloroform | Bromodichloromethane | Chlorodibromomethane | Bromoform |
|---|---|---|---|---|
| Range (µg/L) | 0.86 - 550 | 0.88 - 550 | 0.84 - 550 | 4.8 - 550 |
| Distilled water | | | | |
| Single-analyst precision | SR = 0.10X + 0.13 | SR = 0.15X - 0.05 | SR = 0.16X + 0.06 | SR = 0.19X - 0.25 |
| Overall precision | S = 0.20X + 0.20 | S = 0.23X + 0.15 | S = 0.26X + 0.35 | S = 0.28X + 0.63 |
| Accuracy | X = 0.92C + 0.04 | X = 0.95C - 0.04 | X = 0.99C - 0.08 | X = 1.03C - 1.48 |
| Tap water | | | | |
| Single-analyst precision | SR = 0.11X + 0.03 | SR = 0.15X + 0.18 | SR = 0.18X + 0.13 | SR = 0.23X - 0.05 |
| Overall precision | S = 0.18X + 0.74 | S = 0.22X + 0.38 | S = 0.27X + 0.07 | S = 0.32X + 0.47 |
| Accuracy | X = 1.02C + 0.52 | X = 1.02C + 0.08 | X = 1.04C - 0.16 | X = 1.08C - 1.75 |

X = mean recovery.
C = true value for the concentration.

TABLE 2. SLOPES OF REGRESSION EQUATIONS EXPRESSED AS PERCENTAGES

| Matrix | Chloroform | Bromo-dichloro-methane | Chloro-dibromo-methane | Bromoform |
|---|---|---|---|---|
| Distilled water | | | | |
| % Recovery | 92 | 95 | 99 | 103 |
| % RSD | 20 | 23 | 26 | 28 |
| % RSD-SA | 10 | 15 | 16 | 19 |
| Tap water | | | | |
| % Recovery | 102 | 102 | 104 | 108 |
| % RSD | 18 | 22 | 27 | 32 |
| % RSD-SA | 11 | 15 | 18 | 23 |

standard deviation for single analyst (% RSD-SA) ranged from 10% to 23%; this also is considered to be good. Again, slightly higher values (not statistically significant) are reported for the tap water, and the probable cause is background in the tap water.

A statistical comparison of the effect of the type of water was performed. It indicated no significant difference between water types.

Method 501.1 appears to be rugged. In the hands of twenty laboratories, who used various instruments and varied conditions, the results were satisfactory.

## SECTION 3

## RECOMMENDATIONS

Method 501.1 is acceptable for the analysis of trihalomethanes in drinking water. The accuracy is excellent, while the overall precision and single-analyst precision are considered good.

Care must be taken to eliminate any hot metallic (active) sites in both the gas chromatograph and the detector. These sites can cause breakdown of the compounds, especially bromoform.

Special care must be taken in handling samples and blanks to avoid contamination from the laboratory atmosphere. It is recommended that at least daily checks for contamination be made by the use of appropriate blanks.

Carry-over of the trihalomethane analytes from the analysis of high concentration samples to the next analysis was noted. It is recommended that the purge device be filled with distilled water and purged for 10 minutes after the analysis of samples suspected of containing high concentrations of trihalomethanes.

# SECTION 4

# DESCRIPTION OF STUDY

## SELECTION OF PARTICIPATING LABORATORIES

On 30 June 1980, as prime contractor, Monsanto Research Corporation (MRC) sent requests for quotation (RFQ) to approximately 150 laboratories which had been identified as potential subcontractors for this interlaboratory study. The RFQ contained a Scope of Work, the fixed price allowed for the effort, a description of the projected timing of the required analyses, and a copy of the analytical method. The detailed writeup for Method 501.1 as published by EPA on 15 May 1979 is presented in Appendix 1 of this report. Interested laboratories were asked to respond to the RFQ with the following information:

- Facilities available at the laboratory, including all instrumentation to be used for the study.
- Previous experience in carrying out the types of analyses specified in the Scope of Work for the compounds of interest.
- Handling procedures for working with hazardous and potentially hazardous chemicals.
- The organization and managerial structure of the laboratory, identifying those personnel involved in managing this study.

- The analyst involved in the analyses to be performed, including his/her experience.

- Quality control/quality assurance procedures and good laboratory practices followed by the laboratory.

The proposals received were ranked, and the twenty most qualified laboratories were selected for participation. Table 3 lists the participating laboratories for the EPA Method 501.1 interlaboratory study. Throughout this report, data provided by these laboratories will be identified only by an anonymous code number.

PHASE I - ANALYSIS OF PRESTUDY CONFERENCE SAMPLES

In November 1980, MRC forwarded to each participating laboratory two sealed glass ampuls containing mixed concentrates of the four trihalomethanes in methanol. Also forwarded were procedures for the preparation of stock solution, procedures for the preparation of aqueous calibration standards, and procedures for spiking the waters with the samples in the ampuls. These recommended procedures are presented in Tables 4, 5, and 6. Some notes on Method 501.1 were also sent to each participating laboratory. The notes included the deletion of Sections 2.3, 2.5, 4.2.1.2, 4.2.2, and 9.5 from the published method which were not appropriate for an interlaboratory study.

For those laboratories employing the Tekmar-ALS autosampler, it was recommended that the purging devices be emptied, loaded with 5 mL of organic-free water, and purged for 10 minutes after high-level samples (100 µg/L or greater) or 5 minutes after low-level samples. This precaution is required because the trihalomethanes are often retained in the purging devices and associated plumbing, which can result in sample carry-over during subsequent analyses. Sample carry-over is not a problem in the analysis of successive samples in the autosampler, but it is a problem in the analysis of

TABLE 3. LABORATORIES PARTICIPATING IN EPA METHOD 501.1 INTERLABORATORY STUDY

Acurex Corporation
285 Clyde Avenue
Mountain View, CA 94042

Analytics
Division of CBL
Subsidiary of Rohm & Haas Co.
1415 Rhoadmiller
Richmond, VA 23260

Clayton Environmental Consultants, Inc.
25711 Southfield Road
Southfield, MI

Engineering Science, Inc.
Research and Development Laboratory
600 Bancroft Way
Berkeley, CA 94710

Environmental Research Group, Inc.
117 North First
Ann Arbor, MI 48104

ERCO/Energy Research Co., Inc.
185 Alewife Brook Parkway
Cambridge, MA 02138

Global Geochemistry Corp.
6919 Eton Avenue
Canoga Park, CA 91303

Jacobs Laboratories (formerly PJB Laboratories)
373 South Fair Oaks Avenue
Pasadena, CA 91105

Normandeau Associates, Inc. (formerly Texas Instruments, Inc.)
1710 Firman Drive
Richardson, TX 75081

Northrop Services, Inc.
Environmental Services
P.O. Box 437
Little Rock, AR 72203

O'Brien & Gere Engrs., Inc.
Box 4873
1304 Buckley Road
Syracuse, NY 13221

Orlando Laboratories, Inc.
P.O. Box 8008
90 West Jersey Street
Orland, FL 32806

PedCo Environmental, Inc.
11499 Chester Road
Cincinnati, OH 45246

Serco Laboratories
Sanitary Engineering Laboratories, Inc.
1931 West County Road, C2
Roseville, MN 55113

State of New York
Department of Health
Tower Building
The Governor Nelson A. Rockeller Empire State Plaza
Albany, NY 12201

Technical Services, Inc.
103-7 Stockton Street
P.O. Box 52329
Jacksonville, FL 32201

UBTL, Division of University of Utah Research Institute
520 Wakara Way
Salt Lake City, UT 84108

Versar, Inc.
6621 Electronic Drive
Springfield, VA 22151

Weston Designers Consultants
Weston Way
West Chester, PA 19380

Wilson Laboratories
Analytical & Research Chemists and Biologists
528 North Ninth
Salina, KS 67401

TABLE 4. PROCEDURE FOR PREPARATION OF STOCK SOLUTIONS

1. Place about 9.8 mL of methyl alcohol into a ground glass stoppered 10-mL volumetric flask.

2. Allow the flask to stand unstoppered about 10 minutes or until all alcohol wetted surfaces have dried.

3. Weigh the flask to the nearest 0.1 mg.

4. Using a 100-µL syringe, immediately add 2 drops of the reference standard to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

5. Dilute to volume, stopper, then mix by inverting the flask several times.

6. Transfer the solution to a dated and labeled 15-mL screw-cap bottle with a Teflon® cap liner.

7. Calculate the concentration in micrograms per microliter from the net gain in weight.

8. Store the solution at 4°C.

All standard solutions prepared in methyl alcohol are stable up to 4 weeks when stored under these conditions. They should be discarded after that time has elapsed.

Because of the toxicity of the purgeables, it is necessary to prepare primary dilutions in a hood. It is further recommended that a NIOSH/MESA-approved toxic gas respirator be used when the analyst handles high concentrations of such materials.

TABLE 5. PROCEDURE FOR PREPARATION OF AQUEOUS CALIBRATION STANDARDS

To prepare accurate standard solutions, the following precautions must be observed:

- Do not inject more than 20 µL of alcoholic standards into 100 mL of reagent water.
- Use a 25-µL Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standard into water.)
- Rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as fast as possible after injection.
- Mix aqueous standards by inverting the flask three times only.
- Never use pipets to dilute or transfer samples or aqueous standards.
- Aqueous standards when stored with a headspace are not stable and should be discarded after one hour.

TABLE 6. PROCEDURE FOR SPIKING WATER

If duplicate analyses are to be performed on one ampul, concurrently perform all of the following steps below in duplicate:

- Fill a 100-mL volumetric flask to volume with reagent water.
- Stablize the ampuls to 20°C.
- Use a 25-µL Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standard into water.)
- Open the ampuls by breaking off the top at the break area on the neck and immediately fill the syringe.
- Rapidly inject 20 µL of the ampul concentrate into the expanded area of the filled volumetric flask. Remove the needle as fast as possible after injection.
- Mix the sample by inverting the flask three times only.
- Never use pipets to dilute or transfer samples or aqueous standards.
- Aqueous solutions when stored with a headspace are not stable and should be discarded after one hour.

successive sets of samples. It also was recommended that a blank be run each day to ensure that carry-over is not occurring (ref. Section 3.1 of Method 501.1).

Recommended purge/trap samplers included the Hewlett-Packard with up to a 15-mL purge vessel or the Tekmar with a 5-mL purge vessel. It was recommended that the Tekmar unit with a 25-mL purge vessel not be used (ref. Section 4.1). Other recommendations were as follows:

- The all-Tenax trap is acceptable (ref. Section 4.1.2).
- A 1% SP-1000 on Carbopack B column is to be used (ref. Section 4.2.1.1).
- A 10- to 15-mL screw-cap bottle is acceptable. MRC had found the 10-mL bottle to be preferable (ref. Section 4.8).
- Organic-free water used in preparation of aqueous calibration standards should be obtained fresh each day, because the water tends to pick up chlorinated compounds from the air (ref. Section 5.11).
- The chemical reducing agent was not to be added to any samples prior to analysis (ref. Section 6.3).

Two preliminary samples were sent to the participating laboratories. One contained 50 to 65 µg/L of the four trihalomethanes. The analysis of this sample ensured that the method could be implemented properly by the laboratories. The second sample contained approximately 2 µg/L of the analytes in order to evaluate any method or detection problems under more adverse conditions. The results of these analyses are presented in Table 7.

In Table 7, the data are shown after correction for the blank values of the trihalomethanes in the various laboratories' drinking water. If the value for a compound in the blank was greater than or equal to the value in the sample, ND (not detected) is reported. N-1 statistics were used to calculate the standard deviation where ND was calculated as "0," $<X_i$ was calculated as "$X_i$," and NA (not analyzed) was ignored in the calculations. The "true value" listed for each individual compound is the calculated value of the final concentration in the drinking water after adding the prescribed 20-µL volume of the concentrated spiking solution (delivered in sealed ampuls) to the prescribed 100-mL volume of drinking water.

PHASE II - PRESTUDY CONFERENCE

After analysis of the prestudy conference samples, the analysts from the 20 participating laboratories met in Cincinnati, Ohio, on 15 January 1981 to discuss the EPA Method 501.1, and the following potential problems were identified at this meeting:

- The primary problem associated with Method 501.1 was one of contamination. Difficulties in obtaining "organic-free" water and trihalomethane interferants occurring in drinking water samples were the most common comments from the participating laboratories.

- Another problem noted by most of the laboratories was the carry-over of trihalomethane analytes from the analysis of a high concentrations ample to the next analysis. It was recommended that carry-over could be minimize by filling the purge device with distilled water and purging for 10 minutes before the subsequent analysis of a low trihalomethane sample.

TABLE 7. RESULTS OF PRELIMINARY STUDY OF TRIHALOMETHANES BY PURGE AND TRAP (µg/L)

| Laboratory | Compound | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Chloroform | | Bromodichloro-methane | | Chlorodibromo-methane | | Bromoform | |
| 01 | 51.0 | 6.0 | 47.0 | 8.0 | 49.0 | 2.8 | 47.0 | 4.2 |
| 02 | 45.4 | 1.3 | 48.9 | 1.5 | 67.0 | 2.4 | 52.0 | 2.0 |
| 03 | 50.0 | >60.0 | 52.0 | 3.6 | 80.0 | 3.0 | 44.0 | 0.91 |
| 04[a] | | | | | | | | |
| 05 | 36.1 | 17.2 | 55.3 | 28.1 | 51.2 | 15.9 | 49.0 | 4.4 |
| 06 | 5.5 | 0.25 | 5.7 | 0.07 | 8.2 | 0.14 | 5.6 | 0.18 |
| 07 | 49.6 | 1.18 | 59.9 | 2.20 | 80.0 | 3.81 | 73.0 | 12.7 |
| 08 | 49.0 | 36.0 | 48.0 | 11.0 | 75.0 | 4.0 | 51.0 | 5.0 |
| 09 | 62.0 | 3.2 | 72.0 | 2.6 | 88.0 | 6.0 | 84.0 | 6.1 |
| 10 | 25.0 | 8.7 | 21.0 | ND | 31.0 | ND | 23.0 | ND |
| 11 | 43.0 | 11.0 | 49.0 | 9.5 | 60.0 | 9.7 | 38.0 | 1.0 |
| 12 | 36.0 | 14.0 | 38.0 | 10.0 | 48.0 | 10.0 | 25.0 | 5.2 |
| 13 | 35.2 | 2.0 | 33.2 | 1.6 | 52.2 | 1.7 | 38.8 | 1.7 |
| 14 | 45.0 | 10.0 | 41.0 | 17.0 | 57.0 | 4.9 | 38.0 | 1.3 |
| 15[a] | | | | | | | | |
| 16 | 43.1 | 41.72 | 42.3 | 11.17 | 53.5 | 6.70 | 34.9 | 2.41 |
| 17 | 30.11 | 12.57 | 18.16 | 13.11 | 52.36 | 3.09 | 106.5 | 3.15 |
| 18[a] | | | | | | | | |
| 19[a] | | | | | | | | |
| 20[a] | | | | | | | | |
| True value | 50.0 | 2.0 | 50.0 | 2.0 | 64.0 | 2.6 | 50.0 | 2.0 |
| Mean[b] | 40.4 | 15.0 | 42.1 | 8.0 | 56.8 | 4.9 | 47.3 | 3.4 |
| Standard deviation | 13.0 | 17.0 | 17.0 | 7.7 | 20.0 | 4.1 | 25.0 | 3.2 |
| Range | 5.5-62 | 0.25->60 | 5.7-72 | ND-28.1 | 8.2-88 | ND-15.9 | 5.6-106.5 | ND-12.7 |

[a]No data reported by these laboratories.

[b]Data reported as "not detected" was calculated as 0. Data reported as $<X_i$ was calculated as $X_i$.

Preliminary to the study conference, MRC analysts conducted a study on the precision of Method 501.1 at nominal trihalomethane concentrations from 1 µg/L to 1,500 µg/L. The precision study constituted the analysis of seven replicates of each of the four trihalomethanes in organic-free water at seven nominal concentrations. Table 8 presents the percent relative standard deviations obtained in this study. At the 1000 and 1500 µg/L concentrations, detector satuation was observed for all of the analytes except bromoform. As a result of this observation, the highest concentrations of trihalomethanes employed in the interlaboratory study was limited to 550 µg/L. Detailed results of this test are presented in Appendix B.

TABLE 8. METHOD 501.1 PRECISION

| Nominal concentration, µg/L | Relative standard deviation, % | | | |
|---|---|---|---|---|
| | Chloroform | Bromodichloro-methane | Chlorodibromo-methane | Bromoform |
| 1 | 13 | 11 | 5.7 | 10 |
| 50 | 5.5 | 4.4 | 4.8 | 5.3 |
| 140 | 4.1 | 3.7 | 2.0 | 3.0 |
| 250 | 3.3 | 2.6 | 1.7 | 1.3 |
| 500 | 6.0 | 3.9 | 2.6 | 3.9 |
| 1,000[a] | 0.8 | 0.6 | 1.5 | 1.6 |
| 1,500[a] | 3.0 | 1.2 | 2.4 | 2.8 |

[a]Detector saturation observed at these concentrations.

## PHASE III - INTERLABORATORY METHOD STUDY

Method study samples were sent to participating laboratories in March 1981. The design of the method study was based on Youden's original plan [1] for the collaborative evaluation of precision and accuracy for analytical methods. According to Youden's design, samples are analyzed in pairs instead of in duplicate, and each sample of a pair has slightly different concentrations of the constituents. The analyst is directed to perform a single analysis and report <u>one</u> value for each sample.

Six spiking solutions were made such that three different concentration ranges were each represented by two different solutions (Youden pairs). Solution numbers 1 and 2 had trihalomethanes at low levels of about 1 µg/L. Solution numbers 3 and 4 had concentrations near the drinking water standards of 50 µg/L. Solutions 5 and 6 contained trihalomethanes at levels about ten times the intermediate levels. Table 9 shows the calculated trihalomethane concentrations for each spiked solution.

The concentrated spiking solutions were sealed in glass ampuls employing a Cozzoli Model HS1 ampul sealer. Verification of the concentrations of the trihalomethanes in the ampuls shipped to the participating laboratories was conducted by both MRC and the Quality Assuranch Branch of EMSL, EPA. Method 501.2 was employed by MRC while the direct injestion GC/MS was used by EPA. The combined data indicated that the ampuls were correctly prepared. The mean recoveries of the participating laboratories also support the verification of the ampuls. Verification results are presented in Appendix C.

TABLE 9. TRIHALOMETHANE CONCENTRATIONS IN SPIKED SOLUTIONS (µg/L)

| Concentration | Chloroform | Bromodichloro-methane | Chlorodibromo-methane | Bromoform |
|---|---|---|---|---|
| 1 | 0.862 | 0.878 | 0.844 | 4.84 |
| 2 | 1.14 | 1.16 | 1.15 | 5.93 |
| 3 | 46.0 | 46.0 | 46.0 | 45.8 |
| 4 | 54.1 | 54.4 | 54.3 | 54.0 |
| 5 | 550 | 550 | 550 | 550 |
| 6 | 450 | 450 | 450 | 450 |

The participating laboratories were again given copies of the recommended procedures for preparation of stock solutions, calibration standards and quality control samples that had been given

to the laboratories prior to the prestudy conference. A questionnaire also was provided to all participating laboratory. Each laboratory was directed to spike individual drinking water samples from their laboratory with 20 µL of each of the following ampuls and to analyze a drinking water blank:

| | | |
|---|---|---|
| 501.1 Conc. 1 | 501.1 Conc. 2 | 501.1 Conc. 3 |
| 501.1 Conc. 4 | 501.1 Conc. 5 | 501.1 Conc. 6 |

Each laboratory also was directed to spike individual distilled-water samples from their laboratory with 20 µL of each of the sample ampuls (different ampuls), and to analyze a distilled water blank. Forms were provided for reporting the analytical results in µg/L of all samples using the following significant figure format:

XXX

XX.X

X.XX

0.XX

## SECTION 5

## STATISTICAL TREATMENT OF DATA

Data obtained from the interlaboratory method validation study were subjected to statistical analyses by the Battelle Columbus Laboratories Columbus, Ohio, under EPA Contract 68-03-2624. The analyses were performed employing the Interlaboratory Method Validation Study (IMVS) system [2] of computer programs. This system of programs was designed to implement ASTM procedure D2777, "Standard Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water" [3]. The analyses conducted using the IMVS system included tests for the rejection of outliers (both whole laboratories for a water-type and individual data points), estimation of mean recovery (accuracy), estimation of single-analyst and overall precision, and tests for the effects of water type on accuracy and precision.

### REJECTION OF OUTLIERS

An outlying observation, or "outlier," is a data point that appears to deviate markedly from other members of the sample in which it occurs. Outlying data points are very commonly encountered during interlaboratory test programs; if they are not removed, they can result in a distortion of the accuracy and precision statistics which characterize the analytical method. These outlying points cannot be removed indiscriminantly, however, because they may represent an extreme manifestation of the random variability inherent in the method.

ASTM procedure E178-80, "Standard Practice for Dealing with Outlying Observations" [4] and ASTM procedure D2777-77 [3] present explicit statistical rules and methods for identification of outliers.

Data from outlying laboratories for a particular water type were rejected employing Youden's laboratory ranking test procedure [3, 5] at the 5% level of significance. Data remaining after the laboratory ranking procedure were subjected to individual outlier tests. After all zero, missing, "less than" and "nondetect" data were rejected as outliers, the remaining data were examined using the two-sided Thompson T-test for outlier rejection [6]. All data rejected as outliers for this study are identified by an asterisk in the tables of raw data (Table 4-1 to 4-4, Appendix D).

Youden's Laboratory Ranking Procedure

Using the data for each water type, Youden's laboratory ranking test [3, 5] was performed at the 5% level of significance. The Youden laboratory ranking procedure requires a complete set of data from each laboratory within each water type. Missing data from laboratory i for water type j were replaced by the following procedure. Letting $X_{ijk}$ denote the reported measurement from laboratory i for water type j and concentration level $C_k$, it is assumed that

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk}. \qquad (1)$$

where $\beta_j$ and $\gamma_j$ are fixed parameters which determine the effect of water type j; $L_i$ is the systematic error due to laboratory i, and $\varepsilon_{ijk}$ is the random within laboratory error.

Taking natural logarithms, it follows that

$$\ell n\, X_{ijk} = \ell n\, \beta_j + \gamma_j\, \ell n\, C_k + \ell n\, L_i + \ell n\, \varepsilon_{ijk} \qquad (2)$$

which is a linear regression model with dependent variable $\ell n\, X_{ijk}$ and independent variable $\ell n\, C_k$. (Details and justification for this model are discussed in the section "Comparison of Accuracy and Precision Across Water Types.")

The natural logarithms of the individual laboratory's data were regressed against the natural logarithms of the true concentration levels for the six ampuls in each water type. The predicted values for $\ell n\, X_{ijk}$ were obtained from the regression equation, and the missing values for $X_{ijk}$ were estimated by $X_{ijk} = \exp(\ell n\, X_{ijk})$. (For complete details of this procedure, see Reference 2.)

An example of the use of Youden's laboratory ranking procedure is presented in Table 10, where the rankings of the values for chloroform in water 2 are listed for each laboratory and for ampuls 1 through 6. For 20 laboratories and 6 ampuls, the upper and lower critical limits of the sums of the rankings are 104 and 22. If the sum of the rankings of any laboratories equals or exceeds 104, or is equal to or less than 22, that laboratory's data is rejected for all determinations for that analyte (chloroform) in that water (water 2). From Table 10 it is apparent that the data from Laboratories 19 and 20 must be rejected, with Laboratories 6 and 17 representing borderline cases (these data were retained). The estimated missing data were then removed from the data sets.

Test for Individual Outliers

The data remaining after rejection of all zero, missing, "less than" and "nondetect" data were subjected to an individual outlier test based on calculation of the Thompson T-value [3, 6].

TABLE 10. YOUDEN LABORATORY RANKING PROCEDURE FOR CHLOROFORM DATA IN WATER 2

| Laboratory number | Ranking values | | | | | | Cumulative score |
|---|---|---|---|---|---|---|---|
| | Ampul 1 | Ampul 2 | Ampul 3 | Ampul 4 | Ampul 5 | Ampul 6 | |
| 1 | 11 | 9 | 13 | 16 | 11 | 4 | 64 |
| 2 | 9.5 | 14 | 9 | 10 | 5 | 5 | 62.5 |
| 3 | 4 | 1 | 8 | 3 | 8 | 13 | 37 |
| 4 | 12 | 5 | 6 | 15 | 10 | 12 | 60 |
| 5 | 17.5 | 17.5 | 14 | 14 | 15 | 14 | 92 |
| 6 | 17.5 | 17.5 | 18 | 18 | 16 | 15 | 102[b] |
| 7 | 7 | 8 | 5 | 11 | 13.5 | 9 | 53.5 |
| 8 | 1 | 17.5 | 12 | 19 | 18 | 18 | 85.5 |
| 9 | 8 | 7 | 15 | 6 | 6 | 6 | 48 |
| 10 | 17.5 | 13 | 7 | 8 | 3 | 10 | 58.5 |
| 11 | 2 | 4 | 4 | 7 | 12 | 17 | 46 |
| 12 | 17.5 | 17.5 | 16 | 13 | 7 | 8 | 79 |
| 13 | 6 | 10 | 17 | 5 | 17 | 16 | 71 |
| 14 | 13 | 12 | 10 | 12 | 13.5 | 7 | 67.5 |
| 15 | 9.5 | 3 | 20 | 17 | 9 | 11 | 67.5 |
| 16 | 17.5 | 17.5 | 11 | 9 | 19 | 19 | 93[b] |
| 17 | 5 | 6 | 3 | 2 | 4 | 3 | 23[b] |
| 18 | 17.5 | 17.5 | 2 | 4 | 2 | 2 | 45 |
| 19 | 14 | 11 | 19 | 20 | 20 | 20 | 104[a] |
| 20 | 3 | 2 | 1 | 1 | 1 | 1 | 9[a] |

[a]Laboratories rejected versus upper and lower criteria of 104 and 22.

[b]Borderline laboratories.

In these calculations the mean recovery, $\bar{x}$, is given by

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \qquad (3)$$

and the standard deviations, s, is given by

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2} \qquad (4)$$

where $x_i$ = individual analyses
n = number of retained analyses values in the ampul set

Thompson's T is defined as:

$$T = \frac{x_e - \bar{x}}{s} \qquad (5)$$

where $x_e$ is the retained $x_i$ value farthest away from the mean ($\bar{x}$) of the set of retained data.

The outlier may be rejected if the value of T calculated exceeds the critical value for T (two-sided test) as presented in Table 11. The 5% significance level was employed. If the extreme value is rejected as an outlier, the test is repeated for the next extreme value among the data until the value being tested is less than the critical T-value.

TABLE 11. CRITICAL VALUES FOR THOMPSON'S T (TWO-SIDED TEST) WHEN STANDARD DEVIATION IS CALCULATED FROM THE SAME SAMPLES

| Number of observations, n | 5% significance level |
|---|---|
| 7 | 2.02 |
| 8 | 2.13 |
| 9 | 2.21 |
| 10 | 2.29 |
| 11 | 2.36 |
| 12 | 2.41 |
| 13 | 2.46 |
| 14 | 2.51 |
| 15 | 2.55 |
| 16 | 2.58 |
| 17 | 2.62 |
| 18 | 2.65 |
| 19 | 2.68 |
| 20 | 2.71 |

TABLE 12. RESULTS OF TEST FOR INDIVIDUAL OUTLIERS (CHLOROFORM IN WATER 2)

| Ampul | Lab | Extreme Value $x_e$ | Mean $\bar{x}$ | Standard deviation $s$ | Calculated T $\frac{x_e - \bar{x}}{s} = T$ | Number of points $n$ | Critical T $T_c$ | Decision |
|---|---|---|---|---|---|---|---|---|
| 1 | 8 | 15.60 | 2.44 | 4.21 | 3.13 | 12 | 2.41 | Reject |
| 2 | 3 | 17.70 | 3.27 | 4.77 | 3.03 | 12 | 2.41 | Reject |
| 3 | 18 | 69.20 | 45.77 | 7.90 | 2.97 | 17 | 2.62 | Reject |
| 3 | 6 | 29.20 | 44.77 | 5.68 | 2.74 | 16 | 2.58 | Reject |
| 5 | 16 | 155.0 | 527.9 | 121.3 | 3.07 | 18 | 2.65 | Reject |
| 6 | 16 | 145.0 | 440.4 | 108.0 | 2.73 | 18 | 2.65 | Reject |

As shown in Table 12 six additional data points are identified as outliers by Thompson's T-test for the illustrative example of the analyte chloroform in water 2. In summary, of the original 120 data points for chloroform in water 2 (20 laboratories x 6 ampuls), all data points for laboratories 19 and 20 were rejected on the basis of Youden's laboratory ranking procedure (total of 12 points), and six additional data points were found to be outliers based on the Thompson T-test (for a total of the 18 data points that are identified by an asterisk as outliers in Table 4-1). These same tests were applied for all other analytes in both waters.

STATISTICAL SUMMARIES

After the outlier rejection tests were performed, the following summary statistics were calculated employing the remaining data for each ampul (single analyte, single concentration, single water matrix):

- Number of retained data points, n
- Mean recovery of retained data, $\bar{x}$
- Accuracy as a percent of relative error, % R.E.

- Overall absolute standard deviation, s
- Percent relative overall standard deviation, % RSD
- Absolute single-analyst standard deviation, $s_r$
- Percent relative single-analyst standard deviation, % RSD-SA

All of these statistics, except the single-analyst absolute and relative standard deviations, were calculated using the retained data for each ampul. The basic statistical formulas used for these calculations are given below, where $X_1$, $X_2$,..., $X_n$ denote the values for the n retained data points for a given ampul.

Mean Recovery ($\bar{X}$):

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \qquad (3)$$

Accuracy as a % Relative Error:

$$\% \text{ RE} = \frac{\bar{X} - \text{true value}}{\text{true value}} \times 100 \qquad (6)$$

Overall Standard Deviation:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - \bar{X})^2} \qquad (4)$$

and

Percent Relative Overall Standard Deviation:

$$\% \text{ RSD} = \frac{S}{\bar{X}} \times 100 \qquad (7)$$

The overall standard deviation, S, indicates the precision associated with measurements generated by a group of laboratories. This represents the broad variation in the data collected in a collaborative study. A measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This single-analyst precision, denoted by $S_r$, is measured by

$$S_r = \sqrt{\frac{1}{2(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2} \qquad (8)$$

where $m$ = number of retained Youden-paired observations
$D_i$ = difference between observations in the $i^{th}$ pair
$\bar{D}$ = average of $D_i$ values

The Youden-pair design employed in this study permits the calculation of this single-analyst precision without making duplicate measurements on the same sample. This helps to avoid the well-intentioned manipulation of data that can occur when laboratories make duplicate analyses.

The percent relative standard deviation for the single-analyst precision is calculated by

$$\% \text{ RSD-SA} = \frac{S_r}{\bar{X}^*} \times 100 \qquad (9)$$

where $\bar{X}^*$ is the average of the two mean recoveries corresponding to the two ampuls defining the particular Youden pair. These summary statistics are presented in Tables 13 through 16 for each of the four trihalomethanes in the two water matrices.

TABLE 13. STATISTICAL SUMMARY FOR CHLOROFORM ANALYSES BY WATER TYPE

| | | WATER 1 | | WATER 2 | |
|---|---|---|---|---|---|
| LOW YOUDEN PAIR | | 1 | 2 | 1 | 2 |
| NUMBER OF DATA POINTS | | 17 | 17 | 11 | 11 |
| TRUE VALUE UG/L | | 0.86 | 1.14 | 0.86 | 1.14 |
| MEAN RECOVERY | | .93 | 1.09 | 1.24 | 1.95 |
| ACCURACY AS % REL ERROR | | -3.17 | -4.64 | 43.94 | 71.37 |
| OVERALL STD DEV (S) | | .35 | .46 | .79 | 1.52 |
| OVERALL REL STD DEV, % | | 41.37 | 41.94 | 63.96 | 77.90 |
| SINGLE ANALYST | STD DEV, (SR) | .22 | | 1.00 | |
| | REL DEV, % | 22.80 | | 62.63 | |
| MEDIUM YOUDEN PAIR | | 3 | 4 | 3 | 4 |
| NUMBER OF DATA POINTS | | 17 | 16 | 15 | 18 |
| TRUE VALUE UG/L | | 46.00 | 54.10 | 46.00 | 54.10 |
| MEAN RECOVERY | | 45.06 | 52.21 | 45.77 | 55.12 |
| ACCURACY AS % REL ERROR | | -2.03 | -3.50 | -.49 | 1.88 |
| OVERALL STD DEV (S) | | 4.85 | 4.51 | 3.94 | 13.85 |
| OVERALL REL STD DEV, % | | 10.77 | 8.64 | 8.60 | 25.14 |
| SINGLE ANALYST | STD DEV, (SR) | 4.31 | | 7.90 | |
| | REL DEV, % | 8.87 | | 15.66 | |
| HIGH YOUDEN PAIR | | 5 | 6 | 5 | 6 |
| NUMBER OF DATA POINTS | | 19 | 18 | 17 | 17 |
| TRUE VALUE UG/L | | 550.00 | 450.00 | 550.00 | 450.00 |
| MEAN RECOVERY | | 464.48 | 406.56 | 549.89 | 457.76 |
| ACCURACY AS % REL ERROR | | -15.55 | -9.65 | -.02 | 1.73 |
| OVERALL STD DEV (S) | | 167.01 | 95.95 | 80.24 | 81.41 |
| OVERALL REL STD DEV, % | | 35.96 | 23.62 | 14.59 | 17.79 |
| SINGLE ANALYST | STD DEV, (SR) | 46.99 | | 40.94 | |
| | REL DEV, % | 10.79 | | 8.13 | |

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER

TABLE 14. STATISTICAL SUMMARY FOR BROMODICHLOROMETHANE ANALYSES BY WATER TYPE

| | WATER 1 | | WATER 2 | |
|---|---|---|---|---|
| LOW YOUDEN PAIR | 1 | 2 | 1 | 2 |
| NUMBER OF DATA POINTS | 17 | 15 | 14 | 12 |
| TRUE VALUE UG/L | 0.88 | 1.16 | 0.88 | 1.14 |
| MEAN RECOVERY | .94 | .84 | .92 | 1.39 |
| ACCURACY AS % REL ERROR | -4.40 | -15.95 | 4.38 | 19.47 |
| OVERALL STD DEV (S) | .40 | .29 | .61 | .64 |
| OVERALL REL STD DEV, % | 48.09 | 30.04 | 66.60 | 45.99 |
| SINGLE ANALYST STD DEV, (SR) | .09 | | .35 | |
| SINGLE ANALYST REL DEV, % | 9.85 | | 30.92 | |
| MEDIUM YOUDEN PAIR | 3 | 4 | 3 | 4 |
| NUMBER OF DATA POINTS | 18 | 17 | 17 | 18 |
| TRUE VALUE UG/L | 46.00 | 54.40 | 46.00 | 54.40 |
| MEAN RECOVERY | 46.12 | 53.10 | 48.05 | 57.53 |
| ACCURACY AS % REL ERROR | .25 | -2.39 | 4.45 | 5.75 |
| OVERALL STD DEV (S) | 6.72 | 6.23 | 6.49 | 9.35 |
| OVERALL REL STD DEV, % | 14.57 | 11.74 | 13.93 | 16.25 |
| SINGLE ANALYST STD DEV, (SR) | 5.14 | | 5.00 | |
| SINGLE ANALYST REL DEV, % | 10.36 | | 9.47 | |
| HIGH YOUDEN PAIR | 5 | 6 | 5 | 6 |
| NUMBER OF DATA POINTS | 18 | 18 | 18 | 18 |
| TRUE VALUE UG/L | 550.00 | 450.00 | 550.00 | 450.00 |
| MEAN RECOVERY | 483.50 | 428.67 | 529.36 | 456.89 |
| ACCURACY AS % REL ERROR | -12.09 | -4.74 | -3.75 | 1.53 |
| OVERALL STD DEV (S) | 187.05 | 122.68 | 181.98 | 124.72 |
| OVERALL REL STD DEV, % | 38.69 | 28.62 | 34.38 | 27.30 |
| SINGLE ANALYST STD DEV, (SR) | 91.67 | | 105.89 | |
| SINGLE ANALYST REL DEV, % | 20.10 | | 21.47 | |

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER

TABLE 15. STATISTICAL SUMMARY FOR CHLORODIBROMOMETHANE ANALYSIS BY WATER TYPE

| | | WATER 1 | | WATER 2 | |
|---|---|---|---|---|---|
| LOW YOUDEN PAIR | | 1 | 2 | 1 | 2 |
| NUMBER OF DATA POINTS | | 16 | 17 | 12 | 13 |
| TRUE VALUE UG/L | | 0.84 | 1.15 | 0.84 | 1.15 |
| MEAN RECOVERY | | .71 | 1.15 | .77 | .95 |
| ACCURACY AS % REL ERROR | | -15.65 | .36 | -9.16 | -17.26 |
| OVERALL STD DEV (S) | | .45 | .82 | .27 | .33 |
| OVERALL REL STD DEV, % | | 65.31 | 71.23 | 35.76 | 34.68 |
| SINGLE ANALYST | STD DEV, (SR) | .21 | | .29 | |
| | REL DEV, % | 22.54 | | 33.65 | |
| MEDIUM YOUDEN PAIR | | 3 | 4 | 3 | 4 |
| NUMBER OF DATA POINTS | | 18 | 19 | 19 | 19 |
| TRUE VALUE UG/L | | 46.00 | 54.30 | 46.00 | 54.30 |
| MEAN RECOVERY | | 44.36 | 53.79 | 44.94 | 55.05 |
| ACCURACY AS % REL ERROR | | -3.57 | -.93 | -.08 | 3.03 |
| OVERALL STD DEV (S) | | 6.71 | 9.97 | 12.47 | 10.44 |
| OVERALL REL STD DEV, % | | 15.14 | 19.54 | 27.53 | 18.67 |
| SINGLE ANALYST | STD DEV, (SR) | 6.39 | | 7.93 | |
| | REL DEV, % | 13.01 | | 15.55 | |
| HIGH YOUDEN PAIR | | 5 | 6 | 5 | 6 |
| NUMBER OF DATA POINTS | | 19 | 19 | 19 | 19 |
| TRUE VALUE UG/L | | 550.00 | 450.00 | 550.00 | 450.00 |
| MEAN RECOVERY | | 528.43 | 467.26 | 574.43 | 469.79 |
| ACCURACY AS % REL ERROR | | -3.89 | 3.84 | 4.80 | 10.84 |
| OVERALL STD DEV (S) | | 199.52 | 124.14 | 205.74 | 124.46 |
| OVERALL REL STD DEV, % | | 37.74 | 27.00 | 35.70 | 24.95 |
| SINGLE ANALYST | STD DEV, (SR) | 94.40 | | 113.92 | |
| | REL DEV, % | 18.94 | | 21.19 | |

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER

TABLE 16. STATISTICAL SUMMARY FOR BROMOFORM ANALYSES BY WATER TYPE

| | | WATER 1 | | WATER 2 | |
|---|---|---|---|---|---|
| LOW YOUDEN PAIR | | 1 | 2 | 1 | 2 |
| NUMBER OF DATA POINTS | | 16 | 16 | 14 | 15 |
| TRUE VALUE UG/L | | 4.84 | 5.93 | 4.84 | 5.93 |
| MEAN RECOVERY | | 3.53 | 4.41 | 3.59 | 4.57 |
| ACCURACY AS % REL ERROR | | -26.98 | -22.31 | -24.98 | -22.86 |
| OVERALL STD DEV (S) | | 1.70 | 1.79 | 1.57 | 2.03 |
| OVERALL REL STD DEV, % | | 48.07 | 39.98 | 43.93 | 44.29 |
| SINGLE ANALYST | STD DEV, (SR) | .54 | | .89 | |
| | REL DEV, % | 13.30 | | 21.81 | |
| MEDIUM YOUDEN PAIR | | 3 | 4 | 3 | 4 |
| NUMBER OF DATA POINTS | | 19 | 18 | 19 | 18 |
| TRUE VALUE UG/L | | 45.80 | 54.00 | 45.80 | 54.00 |
| MEAN RECOVERY | | 45.55 | 53.09 | 41.92 | 55.13 |
| ACCURACY AS % REL ERROR | | -.54 | -1.70 | -8.70 | 2.09 |
| OVERALL STD DEV (S) | | 15.42 | 7.98 | 14.91 | 9.18 |
| OVERALL REL STD DEV, % | | 33.86 | 15.04 | 35.61 | 16.65 |
| SINGLE ANALYST | STD DEV, (SR) | 8.19 | | 11.10 | |
| | REL DEV, % | 16.62 | | 22.84 | |
| HIGH YOUDEN PAIR | | 5 | 6 | 5 | 6 |
| NUMBER OF DATA POINTS | | 19 | 19 | 19 | 19 |
| TRUE VALUE UG/L | | 550.00 | 450.00 | 550.00 | 450.00 |
| MEAN RECOVERY | | 550.59 | 489.00 | 610.44 | 529.16 |
| ACCURACY AS % REL ERROR | | .11 | 7.79 | 10.99 | 17.59 |
| OVERALL STD DEV (S) | | 226.51 | 121.26 | 252.49 | 159.99 |
| OVERALL REL STD DEV, % | | 40.05 | 25.00 | 41.40 | 31.94 |
| SINGLE ANALYST | STD DEV, (SR) | 109.47 | | 131.74 | |
| | REL DEV, % | 21.14 | | 23.12 | |

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER

## REGRESSION ANALYSIS OF BASIC STATISTICS

Systematic relationships frequently exist between the mean recovery statistics and the true concentration levels across ampuls, and between the precision statistics and the mean recovery statistics. Given a plot of precision values versus concentration levels, a smooth curve drawn through the points can show that the precision is found to (1) be constant and not vary with level, (2) vary directly with level in a linear manner; or (3) vary with level in a curvilinear fashion.

In order to derive statements for method accuracy and precision, the basic statistics were regressed assuming linear relationships, fitting the data to a line using weighted least-squares. The weights were chosen to be inversely related to the true concentration in the case of accuracy and inversely related to the mean recovery in the case of precision. The inverse weightings were employed to minimize skewing created by the high Youden-pair data. The results of the regression analyses are discussed below.

### Statements of Method Accuracy

The accuracy of Method 501.1 is characterized by comparing the mean recovery of the analyte, $\bar{X}$, to the true concentration level of the compound, C, in the ampul. The IMVS program conducts these calculations via matrix algebra, where weighted least-squares linear regression of $\bar{X}$ versus C is conducted with weights chosen to be inversely related to the square of the true concentration levels (see page 108 of Reference 2 for details). This method is equivalent to that suggested by Britton [7] where the linear regression for $\bar{X}$ versus C is achieved by using the customary least-squares algorithm to fit:

$$\frac{\bar{X}}{C} = a + b\left(\frac{1}{C}\right) \qquad (10)$$

which can then be converted to the desired relationships by multiplying through by C, giving:

$$\bar{X} = aC + b \qquad (11)$$

These equations were presented earlier in Table 1.

If the intercept (b) associated with the fitted line is negligible (i.e., essentially zero), then the slope (a) provides a unique value which represents the percent recovery over all of the concentration levels.

Statements of Method Precision

The precision of Method 501.1 is characterized by comparing the overall and single-analyst standard deviations to the mean recovery, $\bar{X}$. The IMVS program conducts these calculations via matrix algebra, where a weighted least-squares linear regression of S and $S_r$ versus $\bar{X}$ is conducted with weights chosen to be inversely proportional to the square of the mean recovery (see page 108 of Reference 2, for details). This method is equivalent to that suggested by Britton [7] where the linear regressions for S and $S_r$ versus C are achieved by using the customary least-squares procedure to fit the equations,

$$\frac{S}{C} = c + d\left(\frac{1}{C}\right) \qquad (12)$$

In this study, however, the regression was conducted versus $\bar{X}$ as follows:

$$\frac{S}{\bar{X}} = c + d\left(\frac{1}{\bar{X}}\right) \qquad (13)$$

which is then converted by multiplying through by $\bar{X}$ to yield the linear relationships

$$S = a\bar{X} + b \tag{14}$$

and

$$S_r = c\bar{X} + d \tag{15}$$

These equations were also presented earlier in Table 1.

If the intercepts, b and d, are negligible, then the slopes, a and c, are good approximations to the overall and single-analyst percent relative standard deviations, respectively. These, in turn, are measures of the method precision.

As a test of the relative magnitudes of the intercept values, average values of S, $S_r$, and $\bar{X}$ were calculated from the data in Tables 13 through 16 over the three concentration levels reported in this study. In only the following three of twenty-four cases did the intercept values in Table 1 exceed one percent (considered negligible) of these average values:

- S for bromoform in distilled water (intercept 1.03% of averaged value)
- $S_r$ for chloroform in tap water (intercept 5.0% of averaged value)
- S for chloroform in tap water (intercept 2.4% of averaged value)

## COMPARISON OF ACCURACY AND PRECISION ACROSS WATER TYPES

It is possible that the accuracy and precision of Method 501.1 depend upon the type of water being analyzed. The summary statistics $\bar{X}$, S, and $S_r$ are calculated separately for each concentration level within each water type. They can be compared across water types in order to obtain information about the effects of water type on accuracy and precision. However, the use of these summary statistics in this manner has several disadvantages. First, it is cumbersome because there are 12 mean recovery statistics ($\bar{X}$) (6 ampuls x 2 waters), 12 precision statistics (S), and 6 precision statistics ($S_r$) calculated for each compound. Comparison of these statistics across concentration levels and across water types becomes unwieldy. Second, the statistical properties of this type of comparison procedure are difficult to determine. Finally, due to variation associated with $\bar{X}$, S, and $S_r$, comparisons based on these statistics can lead to inconsistent conclusions about the effect of water type. For example, distilled water may produce a significantly lower value than drinking water for the precision statistic S at a high concentration, but a significantly higher value for S at a low concentration.

An alternative approach, described in detail in Reference 2, has been developed to test for the effects of water type. This alternative approach is based on the concept of summarizing the average effect of water type across concentration levels rather than studying the local effects at each concentration level. If significant differences are established by this alternative technique, then the summary statistics can be used for further local analysis.

Thus, in order to check for the effect of water type on the analytical results, first a global F-test of the accuracy and precision is calculated. If the global F-test shows no water type

effects, no further calculations are required. If the F-test shows significance of water type, calculations are performed to determine if the individual differences are statistically significant by calculating a confidence interval for the difference between water type. A statistical significance is established if at least one of the confidence intervals for the differences does not include zero. Even if a statistical sgnicifance of water type is established, the effect may not have any statistically significant water type effects is related to the size and interpretation of the differences and can be examined by comparing the mean recovery and standard deviation for each water type to the same values for distilled water.

The global F-test for the effect of water type is calculated using the following statistical model. If $X_{ijk}$ denotes the measurement reported by laboratory i, for water type j, and ampul k, then

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \qquad (1)$$

where $i = 1,2,\ldots, 20$
$j = 1,2$
$k = 1,2,\ldots, 6$

Model components $\beta_j$ and $\gamma_j$ are fixed parameters that determine the effect of water type j on the behavior of the observed measurements ($X_{ijk}$). The parameter $C_k$ is the true concentration level associated with ampul k. The model component $L_i$ is a random factor which accounts for the systematic error associated with laboratory i. The model component $\varepsilon_{ijk}$ is the random factor that accounts for the within-laboratory error.

The model is designed to approximate the global behavior of the data. The multiplicative structure was chosen because of two important properties. First, it allows for a possible curvilinear

relationship between the data ($X_{ijk}$) and the true concentration level ($C_k$) through the use of the exponent $\gamma_j$ on $C_k$. This makes the model more flexible in the data and the concentration level $C_k$ in this model. This property is important because it is typical of interlaboratory data collected under conditions where the true concentration levels vary widely.

Accuracy is related directly to the mean recovery or expected value of the measurements ($X_{ijk}$). The expected value for the data modeled by Equation 1 is

$$E(X_{ijk}) = \beta_j \cdot C_k^{\gamma_j} \cdot E(L_i \cdot \varepsilon_{ijk}) \qquad (16)$$

Precision is related to the variability in the measurements ($X_{ijk}$). The variance of the data modeled by Equation 1 is

$$Var(X_{ijk}) = \left[\beta_j \; C_k^{\gamma_j}\right]^2 Var(L_i \cdot \varepsilon_{ijk}), \qquad (17)$$

which is an increasing function of $C_k$. (See Reference 2 for a complete discussion of this model.)

The accuracy and precision of Method 501.1 depend upon water type through Equations 16 and 17 and the parameters $\beta_j$ and $\gamma_j$. If the $\beta_j$ and $\gamma_j$ vary with j (i.e., vary across water type), then the accuracy and precision of the method also vary across water type.

To determine if these parameters do vary across water type and to compare their values, they must be estimated from the laboratory data using regression techniques. Equation 1 represents the basic model. However, taking natural logarithms of both sides of Equation 1, the following straight line regression model is obtained.

$$\ell n\ X_{ijk} = \ell n\ \beta_j + \gamma_j\ \ell n\ C_k + \ell n\ L_i + \ell n\ \varepsilon_{ijk} \qquad (2)$$

The parameter $\ell n\ \beta_j$ is the intercept, and $\gamma_j$ is the slope of the regression line associated with water type j. It is assumed that $\ell n\ L_i$ is normally distributed with mean 0 and variance $\sigma_L^2$, that $\ell n\ \varepsilon_{ijk}$ is normally distributed with mean 0 and variance $\sigma_\varepsilon^2$, and that the $\ell n\ L_i$ and $\ell n\ \varepsilon_{ijk}$ terms are independent.

Based on Equation 2, the comparison of water types reduces to the comparison of straight lines. Distilled water is viewed as a control, and each of the remaining lines is compared directly to the line for distilled water.

Using the data on the log-log scale and regression techniques, the parameter $\ell n\ \beta_j$ (and hence $\beta_j$) and $\gamma_j$ can be estimated. These estimates are then used to formally test the null (no water type effect) versus alternative (water type effect) hypotheses

$$H_0: \quad \ell n\ \beta_j - \ell n\ \beta_1 = 0 \text{ and } \gamma_j - \gamma_1 = 0 \text{ for } j = 2 \qquad (18)$$

versus

$$H_A: \quad \ell n\ \beta_j - \ell n\ \beta_1 \neq 0 \text{ and/or } \gamma_j - \gamma_1 \neq 0 \text{ for some } j = 2 \qquad (19)$$

The null hypothesis ($H_0$) is tested against the alternative hypothesis ($H_A$) using a F-statistic. The probability of obtaining the value of an F-statistic as large as the value which was actually observed, Prob(F > F OBS), is calculated under the assumption that $H_0$ is true. $H_0$ is rejected in favor of $H_A$ if Prob(F > F OBS) is less than 0.05, showing a possible effect due to water type.

If $H_0$ is not rejected, then there is no evidence in the data that the $\beta_j$ vary with j or that the $\gamma_j$ vary with j. Therefore, there is no evidence of an effect due to water type on the accuracy or precision of the method. If $H_0$ is rejected, then some linear combination of the differences ($\ell n\ \beta_j - \ell n\ \beta$) and ($\gamma_j - \gamma_1$) is statistically different from zero. This does not necessarily mean that there is an effect due to water type which is statistically significant. The effect due to water type is judged to be statistically significant only if one of the differences, ($\ell n\ \beta_j - \ell n\ \beta_1$) and/or ($\gamma_j - \gamma_1$), is statistically different from zero. This is determined by checking the simultaneous 95% confidence intervals which are constructed for each of these differences. Each true difference can be stated to lie within its respective confidence interval with 95% confidence. If zero is contained within the confidence interval, then there is no evidence that the corresponding difference is significantly different from zero and no further calculations are required.

If at least one of the confidence intervals for the differences ($\ell n\ \beta_j - \ell n\ \beta_1$) or ($\gamma_j - \gamma_1$) fails to include zero, then the statistical significance of the effect due to water type has been established. Even if a statistically significant effect due to water type were to be established, that would not necessarily mean that the effect would be of practical importance. Practical importance is related to the size and interpretation of the differences. The computer generated data for the point estimates, analysis of variance, and confidence interval are shown in Table 17.

TABLE 17. EFFECT OF WATER TYPE ON ANALYSES

| | Chloroform | Bromodi-chloromethane | Chlorodi-bromomethane | Bromoform |
|---|---|---|---|---|
| **Point estimates** | | | | |
| Distilled slope ($\gamma_1$) | 0.98 | 0.01 | 1.03 | 1.07 |
| Tap water slope ($\ell n\gamma$) | -0.01 | 0.00 | -0.02 | 0.02 |
| Tap water intercept ($\ell n\beta$) | 0.21 | 0.06 | 0.17 | -0.06 |
| **Analysis of variance** | | | | |
| Degrees of freedom | 173 | 182 | 190 | 194 |
| F-value | 4.22 | 0.88 | 1.93 | 0.26 |
| Level of significance | 0.016 | 0.42 | 0.15 | 0.77 |
| Possible water type effect[a] | Yes | No | No | No |
| **95% confidence interval** | | | | |
| Tap water slope[b] | -0.06 to 0.04 | -0.05 to 0.05 | -0.07 to 0.03 | -0.05 to 0.09 |
| Tap water intercept | -0.02 to 0.44 | -0.15 to 0.28 | -0.05 to 0.39 | -0.06 to 0.27 |
| Water type effect[c] | No | No | No | No |

[a]If level of significance is less than 0.05, there is a possible effect of water type.

[b]The slope and intervept estimates are not the same as those from the accuracy and precision regressions.

[c]If zero is contained in the slope and intercept intervals, there is no statistical significance between water types.

## SECTION 6

## RESULTS AND DISCUSSION

The objective of this study was to characterize the performance of Method 501.1 in terms of accuracy, overall precision, single-analyst precision, and the effect of water type on accuracy and precision.

One measure of the performance of the method is that 15% of the 960 data points were rejected as outliers, which is equivalent to rejecting data from three of the twenty laboratories. One-half of the rejected data points were from two of the twenty laboratories (19 and 20). Both of these laboratories did not report analytical results on the prestudy samples.

### ACCURACY

The accuracy of Method 501.1 is obtained by comparing the mean recovery, $\bar{x}$, to the true values of concentration in µg/L. In the statistical summary Tables 13 through 16, individual values of accuracy as percent relative error are listed for each analyte, in each water matrix, and at each of the six concentration levels in that water matrix (three Youden pairs). This results in 48 separate values for the four compounds for accuracy. The weighted linear regression of mean recovery, $\bar{x}$, versus true concentration level, c, provides values representing the percent recovery over all of the concentration levels. This reduces the separate values for accuracy to eight -- one value for each of four analytes in each of two waters. Table 18 presents the percent recovery for each compound in water types as measured by the slopes of the

TABLE 18. PERCENT RECOVERY STATISTICS

| Compound | Slope of regression equation[a] | | Average of mean recovery[b] | |
|---|---|---|---|---|
| | Distilled water | Tap water | Distilled water | Tap water |
| Chloroform | 92 | 102 | 94 | 120 |
| Bromodichloromethane | 95 | 102 | 93 | 105 |
| Chlorodibromomethane | 99 | 104 | 97 | 99 |
| Bromoform | 103 | 108 | 93 | 96 |

[a]From Table5-11.

[b]From Tables 5-7 through 5-10.

weighted linear equations for recovery. This is a simplified approach because the intercept portion of the regression equation is assumed to be insignificant. The values from the slope of the recovery equations are compared to percent recoveries calculated from the average of the quotients $\bar{x}$:c presented in Tables 13 through 16. From Table 18, it is evident that the percent recoveries (or accuracies) calculated by the two methods are in substantial agreement in most cases. The exception is chloroform in tap water. The 120% mean recovery for chloroform actually reflects relatively minor differences occurring at low concentrations (1.0 µg/L true value versus 1.6 µg/L for 160% recovery). The mean recovery of the middle Youden-pair concentrations was 101%, and the mean recovery of the high Youden-pair concentrations was also 101%. In any case, it is apparent that the accuracy of the method based on percent recoveries is excellent.

PRECISION

The overall and single-analyst precisions of Method 501.1 were determined as percent relative standard deviations for each analyte, water type, and concentration level. The statistical

summary Tables 19 through 21 present 48 individual values of overall percent relative standard deviation, and 24 individual values of single-analyst percent relative standard deviation. The weighted linear regression of standard deviation, s, versus mean recovery, $\bar{x}$, provides values of percent relative standard over all of the concentration ranges. This reduces the separate measures of precision to eight -- one value for each of four analytes in each of two water types. Tables 19 and 20 present the percent relative standard deviations as measured by the slopes of the weighted linear regression equations presented earlier in Table 1 for the overall and the single-analyst precision, respectively. These values are compared to the averages of the percent relative standard deviatons presented in Tables 13 through 16. This is a simplified approach because the intercept portion of the regression equation is assumed to be insignificant.

TABLE 19. OVERALL PERCENT RELATIVE STANDARD DEVIATION

| Compound | Slope of regression equation | | Average of percent rel. std. dev. | |
|---|---|---|---|---|
| | Distilled water | Tap water | Distilled water | Tap water |
| Chloroform | 20 | 18 | 27 | 35 |
| Bromodichloromethane | 23 | 22 | 29 | 34 |
| Chlorodibromomethane | 26 | 27 | 39 | 30 |
| Bromoform | 28 | 32 | 34 | 36 |

TABLE 20. SINGLE-ANALYST PERCENT RELATIVE STANDARD DEVIATION

| Compound | Slope of regression equation | | Average of percent rel. std. dev. | |
|---|---|---|---|---|
| | Distilled water | Tap water | Distilled water | Tap water |
| Chloroform | 10 | 11 | 14 | 35 |
| Bromodichloromethane | 15 | 15 | 13 | 21 |
| Chloridibromomethane | 16 | 18 | 18 | 23 |
| Bromoform | 19 | 23 | 17 | 26 |

TABLE 21. SUMMARY OF PRECISION (PERCENT RSD) BY ANALYTE, WATER TYPE, AND CONCENTRATION RANGE

| Water type | Analyte | Low Youden pair | Medium Youden pair | High Youden pair |
|---|---|---|---|---|
| Distilled water | Chloroform | 41.7 | 9.7 | 29.9 |
| | Bromodichloromethane | 39.1 | 13.2 | 33.7 |
| | Chlorodibromomethane | 68.3 | 16.8 | 32.4 |
| | Bromoform | 43.3 | 24.5 | 32.5 |
| | Average of all analytes | 48.1 | 16.1 | 32.1 |
| Drinking water | Chloroform | 70.9 | 16.9 | 16.2 |
| | Bromodichloromethane | 56.3 | 15.1 | 30.8 |
| | Chlorodibromomethane | 35.2 | 23.1 | 30.3 |
| | Bromoform | 44.1 | 27.8 | 36.7 |
| | Average of all analytes | 51.6 | 20.7 | 28.5 |

In general, the linear regression yields a lower percent value, meaning a more precise value. The greatest difference in precision calculated by the two methods occurs for chloroform and especially in tap water. This difference could indicate that the basic assumption, that the intercept is insignificant, is wrong. The differences also could indicate high background levels of chloroform and the subsequent errors in correction.

The preceding regression equations assume a linear relationship between the precision of the data and the concentration of the analytes. A summary of precision values in each of the Youden-pair concentrations is presented in Tables 21 and 22, in order to examine the assumption of a linear relationship. In every case, the best precision is exhibited at the median Youden-pair concentration than that predicted by the slope of the regression line. These results imply that better precision is obtainable

TABLE 22. SUMMARY OF PRECISION (PERCENT RSD-SA)[a] BY ANALYTE, WATER TYPE, AND CONCENTRATION RANGE

| Water type | Analyte | Low Youden pair | Medium Youden pair | High Youden pair |
|---|---|---|---|---|
| Distilled water | Chloroform | 22.8 | 8.9 | 10.8 |
| | Bromodichloromethane | 9.9 | 10.4 | 20.1 |
| | Chlorodibromomethane | 22.5 | 13.0 | 19.0 |
| | Bromoform | 13.3 | 16.6 | 21.1 |
| | Average of all analytes | 17.1 | 12.2 | 17.8 |
| Drinking water | Chloroform | 62.6 | 15.7 | 8.1 |
| | Bromodichloromethane | 30.8 | 9.5 | 21.5 |
| | Chlorodibromomethane | 33.7 | 15.6 | 21.2 |
| | Bromoform | 21.8 | 22.9 | 23.1 |
| | Average of all analytes | 37.2 | 15.9 | 18.5 |

[a]Average of Youden pairs.

near the drinking water standard (medium Youden-pair concentration). The precision at the low concentrations is expected to be not as good as that at higher concentrations. The precision at the high concentrations is reasonable but not as good as at the middle concentrations.

## EFFECTS OF WATER TYPES

The comparison of accuracy and precision across water types was presented in Table 17 and is summarized in Table 23. The observed F values and the probability of exceeding the F values are entered for each of the four analytes. Only in the case of chloroform does the F-test suggest a possible effect due to water type [P(F>observed F) = 0.05].

TABLE 23. SUMMARY OF THE TESTS FOR DIFFERENCES ACROSS WATER TYPES

| Compound | Observed F-value | P[F>observed F] | F-test significant at the 5% level? | Statistical significance established by the 95% confidence limits? |
|---|---|---|---|---|
| Chloroform | 4.22 | 0.02 | Yes | No |
| Bromodichloromethane | 0.88 | 0.42 | No | No |
| Chlorodibromomethane | 1.93 | 0.15 | No | No |
| Bromoform | 0.26 | 0.77 | No | No |

Although statistical significance is indicated by the F-test, the null hypothesis test indicated that no practical effect due to water type has been established because zero is contained within the confidence intervals for both $(\ln\beta_j - \ln\beta_i)$ and $(\gamma_j - \gamma_i)$ for all four compounds.

COMPARISON TO METHOD 501.2

Methods 501.1 and 501.2 are designed to measure the same four trihalomethanes in water, the first by the purge-and-trap technique discussed in this report, and the second by pentane extraction of the water. Table 24 compares the accuracy and precision results from this study to that conducted on Method 501.2 [8].

The percent recovery (accuracy) of the two methods are comparable. The precision of Method 501.2 is better than that of 501.1 for each analyte in each water matrix except for the percent relative overall standard deviation for chloroform and dibromochloromethane in tap water.

TABLE 24. COMPARISON OF ACCURACY AND PRECISION OF METHODS 501.1 AND 501.2

| Matrix | | Analyte | | | |
|---|---|---|---|---|---|
| | | Chloroform | Bromo-dichloromethane | Chloro-dibromomethane | Bromoform |
| Distilled Water | | | | | |
| % Rec. | 501.1 | 92 | 95 | 99 | 103 |
| | 501.2 | 101 | 98 | 102 | 101 |
| % RSD | 501.1 | 20 | 23 | 26 | 28 |
| | 501.2 | 17 | 17 | 16 | 15 |
| % RSD-SA | 501.1 | 10 | 15 | 16 | 19 |
| | 501.2 | 6 | 5 | 7 | 7 |
| Tap Water | | | | | |
| % Rec. | 501.1 | 102 | 102 | 104 | 108 |
| | 501.2 | 103 | 101 | 100 | 103 |
| % RSD | 501.1 | 18 | 22 | 27 | 32 |
| | 501.2 | 26 | 23 | 13 | 16 |
| % RSD-SA | 501.1 | 11 | 15 | 18 | 23 |
| | 501.2 | 8 | 7 | 7 | 8 |

% Rec. = percent recovery, a measure of accuracy.
% RSD = percent relative overall standard deviation.
% RSD-SA = percent relative single-analyst standard deviation.
% RSD and % RSD-SA = precision statistics.

RESPONSE TO QUESTIONNAIRE

Nine of the twenty participating laboratories completed the questionnaire on Method 501.1; five others presented some of the information via memorandums. Of those responding, three laboratories employed a Tracor 560 chromatograph, three used Hewlett-Packard instruments (Models 5710, 5750, and 5730A), two employed Varian chromatographs (Models 3700 and 3740), and one used a Perkin-Elmer Sigma I chromatograph. The majority of the laboratories employed a temperature program of 3 minutes at 45°C, and an 8°C/min rise to 220°C. The final temperature was held for times varying from zero to 18 minutes. Two laboratories started their temperature program at higher temperatures (60°C and 90°C). In every case, helium

carrier gas was employed except for one laboratory which used 5% methane in argon. Most laboratories used a 40 mL/min carrier gas flow, but three used higher flows up to 80 mL/min. Nine of the laboratories employed 8 ft x 2 mm chromatographic columns containing 1% SP 1000 on Carbopak B, 60/80 mesh. One laboratory included an 8-cm precolumn of 3% SP 1000 on 100/120 Supelcoport, and another laboratory employed a 6 ft x 4 mm ID column containing 3% SP 1000 on 100/120 Supelcoport.

Eight of the laboratories used Tracor 700 or 700A Hall Electrolytic Conductivity detectors, while two laboratories employed Coulson detectors from Western Scientific Association. The hydrogen flow rates employed in the detector varied from 20 to 60 mL/min; furnace temperatures ranged from 800 to 900°C. Six laboratories used n-propanol as the electrolyte; another two used 100% $H_2O$ (Coulson detectors), and one used methanol. Electrolyte flow rates ranged from 0.5 to 1.3 cc/min.

Five laboratories employed Tekmar purge-and-trap apparatuses (three automated, two manual). Three laboratories used systems designed and constructed by laboratory personnel; one laboratory used a CDS 310 automatic concentrator. A purge-desorb-bake cycle of 11-4-7 minutes was used by four laboratories. Other cycles included purge times of 12 minutes, desorb times from 3 to 7 minutes, and bake times from 0 to 35 minutes. In every case, helium was used as the carrier gas at a flow rate of 40 mL/min. The trap materials used varied; Tenax alone was used by three laboratories; Tenax, silicia gel and charcoal was used by two laboratories; other combinations including 3% OV-1 were employed by others.

No laboratory reported problems in standards preparation or in conducting the purge-and-trap portion of the analysis. Eight laboratories reported no problem with detection limits, but one laboratory encountered poor detection sensitivity for bromoform.

Another laboratory improved the detection of bromoform by increasing the temperature program to a 2 minute hold at 50°C and a 20°C/min heating rate to 200°C. This was reported to result in a decided sharpening of the bromoform peaks.

On the question of linearity of detector response, one laboratory stated that the response to the brominated compounds was low in standards below 10 ppb. Another lab found the same trend, but stated that linearity was good above 20 ppb. Three other laboratories had difficulties with the linearity of detector response to bromoform, especially at the high concentration ranges (>200 µg/L). Three laboratories reported no problems with linearity.

A wide variety of calibration methods was used by the reporting laboratories. The ranged from employing five concentrations of external standards plus a blank to running one near point concentration. Only one laboratory reported day-to-day variations in detector sensitivity and attributed this to differences in flow rates.

A majority of the respondents indicated that little or no problem was encountered with Method 501.1 beyond those mentioned earlier, including (1) the potential contamination of standards and blanks from the laboratory ambient air, and (2) the necessity to clean the purge-and-trap systems after analysis of high concentration samples. One laboratory used 2.0 mL instead of 5.0 mL in the purge device for high concentrations to bring the detector down to a linear portion of the calibration curve. One laboratory suggested that the method write-up include procedures for handling high concentration level samples.

It can be seen that the allowable adjustable parameters, such as temperature program, purge time, etc., varied over a substantial range. The method was rugged even for unusual variation such as

5% methane in argon as a carrier gas for on electrolytic conductivity detector and 2 mL in the purge vessel. Acceptable results were even generated with 3% SP-1000 as the analytical column. This column in generally considered unacceptable because it is prone to false positive results unless exceptional care is taken to avoid analyte carry-over.

The raw data resulting from the 20 participating laboratories employing EPA Method 501.1 for analysis of the four trihalomethanes in distilled water and drinking water are tabulated in Appendix D. Asterisked values in Tables D-1 to D-4 were rejected as outliers on the basis of statistical tests.

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# APPENDIX A

## THE ANALYSIS OF TRIHALOMETHANES IN FINISHED WATERS BY THE PURGE AND TRAP METHOD

Method 501.1



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# THE ANALYSIS OF TRIHALOMETHANES IN FINISHED WATERS BY THE PURGE AND TRAP METHOD

## Method 501.1

U. S. ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
CINCINNATI, OHIO 45268

November 6, 1979

## Foreword

This method has been prepared by the staff of the Environmental Monitoring and Support Laboratory - Cincinnati, at the request of the Office of Drinking Water. Comments and suggestions offered by the Municipal Environmental Research Laboratory, the Technical Support Division, ODW, and the Health Effects Research Laboratory on the September 9, 1977, draft are gratefully acknowledged.

The procedure represents the current state-of-the-art, but as time progresses improvements are anticipated. Users are encouraged to identify problems and assist in updating the method by contacting the Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268.

## The Analysis of Trihalomethanes in Drinking Water by the Purge and Trap Method

1. Scope

1.1 This method (1) is applicable in the determination of four trihalomethanes, i.e. chloroform, dichlorobromethane, dibromochloromethane, and bromoform in finished drinking water, raw source water, or drinking water in any stage of treatment. The concentration of these four compounds is totaled to determine total trihalomethanes (TTHM).

1.2 For compounds other than the above-mentioned trihalomethanes, or for other sample sources, the analyst must demonstrate the usefulness of the method by collecting precision and accuracy data on actual samples as described (2).

1.3 Although the actual detection limits are highly dependent upon the gas chromatographic column and detector employed, the method can be used over a concentration range of approximately 0.5 to 1500 micrograms per liter.

1.4 Well in excess of 100 different water supplies have been analyzed using this method. Supplementary analyses using gas chromatography mass spectrometry (GC/MS) have shown that there is no evidence of interference in the determination of trihalomethanes (3). For this reason, it is not necessary to analyze the raw source water as is required with the Liquid/Liquid Extraction Method (4).

2. Summary

2.2 Trihalomethanes are extracted by an inert gas which is bubbled through the aqueous sample. The trihalomethanes, along with other

organic constituents which exhibit low water solubility and a vapor pressure significantly greater than water, are efficiently transferred from the aqueous phase to the gaseous phase. These compounds are swept from the purging device and are trapped in a short column containing a suitable sorbent. After a predetermined period of time, the trapped components are thermally desorbed and backflushed onto the head of a gas chromatographic column and separated under programmed conditions. Measurement is accomplished with a halogen specific detector such as electrolytic conductivity or microcoulometric titration.

2.3 Confirmatory analyses are performed using dissimilar columns, or by mass spectrometry (5).

2.4 Aqueous standards and unknowns are extracted and analyzed under identical conditions in order to compensate for extraction losses.

2.5 The total analysis time, assuming the absence of other organohalides, is approximately 35 minutes per sample.

3. Interferences

3.1 Impurities contained in the purge gas and organic compounds outgasing from the plumbing ahead of the trap usually account for the majority of contamination problems. The presence of such interferences are easily monitored as a part of the quality control program. Sample blanks are normally run between each set of samples. When a positive trihalomethane response is noted in the sample blank, the analyst should analyze a method blank. Method blanks are run by charging the purging device with organic-free water and analyzing in the normal manner.

If any trihalomethane is noted in the method blank in excess of 0.4 µg/l, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting the blank values is not recommended. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components should be avoided since such materials generally out-gas organic compounds which will be concentrated in the trap during the purge operation. Such out-gasing problems are common whenever new equipment is put into service; as time progresses, minor out-gasing problems generally cure themselves.

3.2 Several instances of accidental sample contamination have been noted and attributed to diffusion of volatile organics through the septum seal and into the sample during shipment and storage. The sample blank is used as a monitor for this problem.

3.3 For compounds that are not efficiently purged, such as bromoform, small variations in sample volume, purge time, purge flow rate, or purge temperature can affect the analytical result. Therefore, samples and standards must be analyzed under identical conditions.

3.4 Cross-contamination can occur whenever high-level and low-level samples are sequentially analyzed. To reduce this likelihood, the purging device and sample syringe should be rinsed twice between samples with organic-free water. Whenever an unusually concentrated sample is encountered, it is highly recommended that it be followed by a sample blank analysis to ensure that sample cross contamination does not occur. For samples containing large amounts of water soluble materials, it may be necessary to wash out the

purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

3.5 Qualitative misidentifications are a problem in using gas chromatographic analysis. Whenever samples whose qualitative nature is unknown are analyzed, the following precautionary measures should be incorporated into the analysis.

3.5.1 Perform duplicate analyses using the two recommended columns (4.2.1 and 4.2.2) which provide different retention order and retention times for the trihalomethanes and other organohalides.

3.5.2 Whenever possible, use GC/MS techniques which provide unequivocal qualitative identifications (5).

4. Apparatus

4.1 The purge and trap equipment consists of three separate pieces of apparatus: the purging device, trap, and desorber. Construction details for a purging device and an easily automated trap-desorber hybrid which has proven to be exceptionally efficient and reproducible are shown in Figures 1 through 4 and described in 4.1.1 through 4.1.3. An earlier acceptable version of the above-mentioned equipment is described in (1).

4.1.1 Purging Device - Construction details are given in Figure 1 for an all-glass 5 ml purging device. The glass frit installed at the base of the sample chamber allows finely divided gas bubbles to pass through the sample while the

sample is restrained above the frit. Gaseous volumes above the sample are kept to a minimum to eliminate dead volume effects, yet allowing sufficient space for most foams to disperse. The inlet and exit ports are constructed from heavy-walled 1/4-inch glass tubing so that leak-free removable connections can be made using "finger-tight" compression fittings containing Teflon ferrules. The removable foam trap is used to control samples that foam.

4.1.2 Trapping Device - The trap (Figure 2) is a short gas chromatographic column which at <35°C retards the flow of the compounds of interest while venting the purge gas and, depending on which sorbent is used, much of the water vapor. The trap should be constructed with a low thermal mass so that it can be heated to 180°C in less than 1 minute for efficient desorption, then rapidly cooled to room temperature for recycling. Variations in the trap ID, wall thickness, sorbents, sorbent packing order, and sorbent mass could adversely affect the trapping and desorption efficiencies for compounds discussed in this text. For this reason, it is important to faithfully reproduce the trap configurations recommended in Figure 2. Traps containing Tenax only, or combinations of Tenax and other sorbents are acceptable for this analysis.

4.1.3 Desorber assembly - Details for the desorber are shown in Figures 3, and 4. With the 6-port valve in the Purge Sorb position (Figure 3), the effluent from the purging device

passes through the trap where the flow rate of the organics is retarded. The GC carrier gas also passes through the 6-port valve and is returned to the GC. With the 6-port valve in the Purge-Sorb position, the operation of the GC is in no way impaired; therefore, routine liquid injection analyses can be performed using the gas chromatograph. After the sample has been purged, the 6-port valve is turned to the desorb position (Figure 4). In this configuration, the trap is coupled in series with the gas chromatographic column allowing the carrier gas to backflush the trapped materials into the analytical column. Just as the valve is actuated, the power is turned on to the resistance wire wrapped around the trap. The power is supplied by an electronic temperature controller. Using this device, the trap is rapidly heated to 180°C and then maintained at 180°C with minimal temperature overshoot. The trapped compounds are released as a "plug" to the gas chromatograph. Normally, packed columns with theoretical efficiencies near 500 plates/foot under programmed temperature conditions can accept such desorb injections without altering peak geometry. Substituting a non-controlled power supply, such as a manually-operated variable transformer, will provide nonreproducible retention times and poor quantitative data unless Injection Procedure (8.9.2) is used.

4.1.4 Several Purge and Trap Devices are now commercially

available. It is recommended that the following be taken into consideration if a unit is to be purchased:

a. Be sure that the unit is completely compatible with the gas chromatograph to be used for the analysis.

b. Use a 5-ml purging device similar to that shown in Figure 1.

c. Be sure the Tenax portion of the trap meets or exceeds the dimensions shown in Figure 2.

d. With the exception of sample introduction, select a unit that has as many of the purge trap functions automated as possible.

4.2 Gas chromatograph - The chromatograph must be temperature programmable and equipped with a halide specific detector.

4.2.1 Column I is an unusually efficient column which provides outstanding separations for a wide variety of organic compounds. Because of its ability to resolve trihalomethanes from other organochlorine compounds, column I should be used as the primary analytical column (see Table 1 for retention data using this column).

4.2.1.1 Column I parameters: Dimensions - 8 feet long x 0.1 inch ID stainless steel or glass tubing. Packing - 1% SP-1000 on Carbopack-B (60/80) mesh. Carrier Gas - helium at 40 ml/minute. Temperature program sequence: 45°C isothermal for 3 minutes, program at 8°C/minute to 220°C then hold for 15 minutes or until all compounds have eluted.

NOTE: It has been found that during handling, packing, and programming, active sites are exposed on the Carbopack-B packing. This results in tailing peak geometry and poor resolution of many constituents. To correct this, pack the first 5 cm of the column with 3% SP-1000 on Chromosorb-W 60/80 followed by the Carbopack-B packing. Condition the pre-column and the Carbopack columns with carrier gas flow at 220°C overnight. Pneumatic shocks and rough treatment of packed columns will cause excessive fracturing of the Carbopack. If pressure in excess of 60 psi is required to obtain 40 ml/minute carrier flow, then the column should be repacked.

4.2.1.2 Acceptable column equivalent to Column I: Dimensions - 8 feet long x 0.1 inch ID stainless steel or glass tubing. Packing - 0.2% Carbowax 1500 on Carbopack-C (80/100) mesh. Carrier Gas - helium at 40 ml/minute. Temperature program sequence - 60°C isothermal for 3 minutes, program at 8°C/ minute to 160°C, then hold for 2 minutes or until all compounds have eluted.

NOTE: It has been found that during handling, packing, and programming, active sites are exposed on the Carbopack-C packing. This

results in poor resolution of constituents and poor peak geometry. To correct this, place a 1 ft. 0.125 in. OD x 0.1 in. ID stainless steel column packed with 3% Carbowax 1500 on Chromosorb-W 60/80 mesh in series before the Carbopack-C column. Condition the precolumn and the Carbopack columns with carrier gas flow at 190°C overnight. The two columns may be retained in series for routine analyses. Trihalomethane retention times are listed in Table 1.

4.2.2 Column II provides unique organohalide-trihalomethane separations when compared to those obtained from Column I (see Figures 5 and 6). However, since the resolution between various compounds is generally not as good as those with Column I, it is recommended that Column II be used as a qualitative confirmatory column for unknown samples when GC/MS confirmation is not possible.

4.2.2.1 Column II parameters: Dimensions - 6 feet long x 0.1 inch ID stainless steel or glass. Packing - n-octane on Porisil-C (100/120 mesh). Carrier Gas - helium at 40 cc/minute. Temperature program sequence - 50°C isothermal for 3 minutes, program at 6°/minute to 170°C, then hold for 4 minutes or until all compounds have eluted. Trihalomethane retention times are listed in Table 1.

4.3 Sampling containers - 40 ml screw cap vials sealed with Teflon faced silicone septa.

Vials and caps - Pierce #13075 or equivalent.

Septa - Pierce #12722 or equivalent.

4.4 Syringes - 5-ml glass hypodermic with luerlok tip (2 each).

4.5 Micro syringes - 10, 100 µl.

4.6 Micro syringe - 25 µl with a 2" x 0.006" ID needle-Hamilton #702N, or equivalent.

4.7 2-way syringe valve with luer ends (3 each) Hamilton #86570-1FM1, or equivalent.

4.8 Standard storage containers - 15 ml amber screw-cap septum bottles with Teflon faced silicone septa.

Bottles and Caps - Pierce #19830, or equivalent.

Septa - Pierce #12716, or equivalent.

5. Reagents and Materials

5.1 Porous polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2 Three percent OV-1 Chromosorb-W 60/80 mesh.

5.3 1.0% SP-1000 on Carbopack-B (60/80 mesh) available from Supelco.

5.4 n-Octane on Porasil-C (100/120 mesh) available from Waters Associates.

5.5 Three percent SP-1000 on Chromosorb-W (60/80 mesh).

5.6 Free and combined chlorine reducing agent - crystalline sodium thiosulfate, ACS Reagent Grade or sodium sulfite, ACS Reagent Grade.

5.7 Activated carbon - Filtrasorb-200, available from Calgon Corporation, Pittsburgh, PA, or equivalent.

5.8 Organic-free water is defined as water free of interference when employed in the purge and trap analysis.

5.8.1 Organic-free water is generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon. Change the activated carbon bed whenever the concentration of any trihalomethane exceeds 0.4 µg/l.

5.8.2 A Millipore Super-Q Water System or its equivalent may be used to generate organic-free water.

5.8.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle with a Teflon seal.

5.8.4 Test organic free water each day it is used by analyzing according to Section 8.

5.9 Standards[a]

5.9.1 Bromoform - 96% - available from Aldrich Chemical Company.

5.9.2 Bromodichloromethane 97% - available from Aldrich Chemical Company.

5.9.3 Chlorodibromomethane - available from Columbia Chemical Inc., Columbia, S.C.

5.9.4 Chloroform - 99% - available from Aldrich Chemical Company.

[a]As a precautionary measure, all standards must be checked for purity by boiling point determinations or GC/MS assays (5).

5.10 Standard Stock Solutions

5.10.1 Place about 9.8 ml of methyl alcohol into a ground glass stoppered 10 ml volumetric flask.

5.10.2 Allow the flask to stand unstoppered about 10 minutes or until all alcohol wetted surfaces have dried.

5.10.3 Weigh the flask to the nearest 0.1 mg.

5.10.4 Using a 100 µl syringe, immediately add 2 drops of the reference standard to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

5.10.5 Dilute to volume, stopper, then mix by inverting the flask several times.

5.10.6 Transfer the solution to a dated and labeled 15 ml screw cap bottle with a Teflon cap liner.

NOTE: Because of the toxicity of trihalomethanes, it is necessary to prepare primary dilutions in a hood. It is further recommended that a NIOSH/MESA approved toxic gas respirator be used when the analyst handles high concentrations of such materials.

5.10.7 Calculate the concentration in micrograms per microliter from the net gain in weight.

5.10.8 Store the solution at $4^{o}C$.

NOTE: All standard solutions prepared in methyl alcohol are stable up to 4 weeks when stored under these conditions. They should be discarded after that time has elapsed.

5.11 Aqueous Calibration Standard Precautions

5.11.1 In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

a. Do not inject more than 20 µl of alcoholic standards into 100 ml of organic-free water.

b. Use a 25 µl Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

c. Rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as fast as possible after injection.

d. Mix aqueous standards by inverting the flask three times only.

e. Discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask as directed in Section 8.5.

f. Never use pipets to dilute or transfer samples or aqueous standards.

g. Aqueous standards when stored with a headspace are not stable and should be discarded after one hour.

h. Aqueous standards can be stored according to Sections 6.4 and 8.6.

5.11.2 Prepare, from the standard stock solutions, secondary dilution mixtures in methyl alcohol so that a 20 µl

injection into 100 ml of organic-free water will generate a calibration standard which produces a response close (±10%) to that of the sample (See 9.1).

5.11.3 Purge and analyze the aqueous calibration standards in the same manner as the samples.

5.11.4 Other calibration procedures (3) which require the delivery of less than 20 µl of a methanolic standard into a 5.0 ml volume of water already contained in the sample syringe are acceptable only if the methanolic standard is delivered by the solvent flush technique (6).

5.12 Quality Check Standard (2.0 µg/l)

5.12.1 From the standard stock solutions, prepare a secondary dilution in methyl alcohol containing 10 ng/µl of each trihalomethane (See Section 5.10.8 Note).

5.12.2 Daily, inject 20.0 µl of this mixture into 100.0 ml of organic-free water and analyze according to Section 8.

6. Sample Collection and Handling

6.1 The sample containers should have a total volume of at least 25 ml.

6.1.1 Narrow mouth screw cap bottles with the TFE fluorocarbon face silicon septa cap liners are strongly recommended.

6.2 Sample Bottle Preparation

6.2.1 Wash all sample bottles and TFE seals in detergent. Rinse with tap water and finally with distilled water.

6.2.2 Allow the bottles and seals to air dry at room temperature, then place in a 105°C oven for one hour, then allow to cool in an area known to be free of organics.

NOTE: Do not heat the TFE seals for extended periods of time (>1 hour) because the silicone layer slowly degrades at 105°C.

6.2.3 When cool, seal the bottles using the TFE seals that will be used for sealing the samples.

6.3 Sample Stabilization - A chemical reducing agent (Section 5.6) is added to the sample in order to arrest the formation of trihalomethanes after sample collection (3, 7). Do not add the reducing agent to samples when data on maximum trihalomethane formation is desired. If chemical stabilization is employed, the reagent is also added to the blanks. The chemical agent (2.5 to 3 mg/40 ml) is added to the empty sample bottles just prior to shipping to the sampling site.

6.4 Sample Collection

6.4.1 Collect all samples in duplicate.

6.4.2 Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is filled.

6.4.3 Seal the bottles so that no air bubbles are entrapped in it.

6.4.4 Maintain the hermetic seal on the sample bottle until analysis.

6.4.5 Sampling from a water tap.

6.4.5.1 Turn on water and allow the system to flush until the temperature of the water has stabilized. Adjust the flow to about 500 ml/minute and collect duplicate samples from the flowing stream.

6.4.6 Sampling from an open body of water.

6.4.6.1 Fill a 1-quart wide-mouth bottle with sample from a representative area. Carefully fill duplicate sample bottles from the 1-quart bottle as noted in 6.4.2.

6.4.7 If a chemical reducing agent has been added to the sample bottles, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

6.4.8 Sealing practice for septum seal screw cap bottles.

6.4.8.1 Open the bottle and fill to overflowing, place on a level surface, position the TFE side of the septum seal upon the convex sample meniscus and seal the bottle by screwing the cap on tightly.

6.4.8.2 Invert the sample and lightly tap the cap on a solid surface. The absence of entrapped air indicates a successful seal. If bubbles are present, open the bottle, add a few additional drops of sample and reseal the bottle as above.

6.4.9 Blanks

6.4.9.1 Prepare blanks in duplicate at the laboratory by filling and sealing sample bottles with organic-free water just prior to shipping the sample bottles to the sampling site.

6.4.9.2 If the sample is to be stabilized, add an identical amount of stabilization reagent to the blanks.

6.4.9.3 Ship the blanks to and from the sampling site along with the sample bottles.

6.4.9.4 Store the blanks and the samples collected at a given site (sample set) together. A sample set is defined as all the samples collected at a given site (i.e., at a water tretment plant, the duplicate raw source waters, the duplicate finished waters and the duplicate blank samples comprise the sample set).

6.5 When samples have been collected according to Section 6, no measurable loss of trihalomethanes has been detected over extended periods of storage time (3). It is recommended that all samples be analyzed within 14 days of collection.

7. Conditioning Traps

7.1 Condition newly packed traps overnight at 180°C with an inert gas flow of at least 20 ml/min.

7.1.1 Vent the trap effluent to the room, not to the analytical column.

7.2 Prior to daily use, condition traps 10 minutes while backflushing at 180°C. It may be beneficial to routinely condition traps overnight while backflushing at 180°C.

7.2.1 The trap may be vented to the analytical column; however, after conditioning, the column must be programmed prior to use.

8. Extraction and Analysis

8.1 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min.

sample is desorbed, i.e., the column is at the initial 45°C operating temperature. The equipment described in Figure 4 will perform accordingly.

8.9.2 With other types of equipment (see Section 4.1.4 and Reference 1) where the trap is not rapidly heated or is not heated in a reproducible manner, it may be necessary to transfer the contents of the trap into the analytical column at <30°C where it is once again trapped. Once the transfer is complete (4 minutes), the column is rapidly heated to the initial operating temperature for analysis.

8.9.3 If injection procedure 8.9.1 is used and the early eluting peaks in the resulting chromatogram have poor geometry or variable retention times, then Section 8.9.2 should be used.

8.10 After the extracted sample is introduced into the gas chromatograph, empty the gas purging device using the sample introduction syringe, followed by two 5-ml flushes of organic-free water. When the purging device is emptied, leave the syringe valve open allowing the purge gas to vent through the sample introduction needle.

8.11 Analyze each sample and sample blank from the sample set in an identical manner (see Section 6.4.9.4) on the same day.

8.12 Prepare calibration standards from the standard stock solutions (Section 5.10) in organic-free water that are close to the unknown in trihalomethane composition and concentration (Section 9.1). The concentrations should be such that only 20 µl or less of the secondary dilution need be added to 100 ml of organic-free water to

produce a standard at the same level as the unknown.

8.13 As an alternative to Section 8.12, prepare a calibration curve for each trihalomethane containing at least 3 points, two of which must bracket the unknown.

9. Analytical Quality Control

9.1 Analyze the 2 µg/l check sample daily before any samples are analyzed. Instrument status checks and lower limit of detection estimations based upon response factor calculations at five times the noise level are obtained from these data. In addition, response factor data obtained from the 2 µg/l check standard can be used to estimate the concentration of the unknowns. From this information, the appropriate standard dilutions can be determined.

9.2 Analyze the sample blank to monitor for potential interferences as described in Sections 3.1, 3.2, and 3.4.

9.3 Spiked Samples

9.3.1 For laboratories analyzing more than 10 samples a day, each 10th sample should be a laboratory generated spike which closely duplicates the average finished drinking water in trihalomethane composition and concentration. Prepare the spiked sample in organic-free water as described in Section 5.11.

9.3.2 For laboratories analyzing less than 10 samples daily, each time the analysis is performed, analyze at least 1 laboratory generated spike sample which closely duplicates the average finished drinking water in trihalomethane composition and concentration. Prepare the spiked sample

in organic-free water as described in Section 5.11.

9.4 Randomly select and analyze 10% of all samples in duplicate.

9.4.1 Analyze all samples in duplicate which appear to deviate more than 30% from any established norm.

9.5 Maintain an up-to-date log on the accuracy and precision data collected in Sections 9.3 and 9.4. If results are significantly different than those cited in Section 11.1, the analyst should check out the entire analyses scheme to determine why the laboratory's precision and accuracy limits are greater.

9.6 Quarterly, spike an EMSL-Cincinnati trihalomethane quality control sample into organic-free water and analyze.

9.6.1 The results of the EMSL trihalomethane quality control sample should agree within 20% of the true value for each trihalomethane. If they do not then the analyst must check each step in the standard generation procedure to solve the problem (Section 5.9, 5.10, and 5.11).

9.7 Maintain a record of the retention times for each trihalomethane using data gathered from spiked samples and standards.

9.7.1 Daily calculate the average retention time for each trihalomethane and the variance encountered for the analyses.

9.7.2 If individual trihalomethane retention time varies by more than 10% over an eight hour period or does not fall with 10% of an established norm, the system is "out of control." The source of retention data variantion must be corrected before acceptable data can be generated.

10. Calculations

10.1 Locate each trihalomethane in the sample chromatogram by comparing the retention time of the suspect peak to the data gathered in 9.7.1. The retention time of the suspect peak must fall within the limits established in 9.7.1 for single column identification.

10.2 Calculate the concentration of the samples by comparing the peak height or peak areas of the samples to the standard peak height (8.12). Round off the data to the nearest µg/l or two significant figures.

$$\mu g/l = \left(\frac{\text{peak height sample}}{\text{peak height standard}}\right) \times (\text{conc. std. } \mu g/l)$$

10.3 Report the results obtained from the lower limit of detection estimates along with the data for the samples.

10.4 Calculate the total trihalomethane concentration (TTHM) by summing the 4 individual trihalomethane concentrations in µg/l.

TTHM (µg/l) = (Conc. $CHCl_3$)+(Conc. $CHBrCl_2$)+(Conc. $CHBr_2Cl$)+ Conc. CHBr).

10.5 Calculate the limit of detection (LOD) for each trihalomethane not detected using the following criteria:

$$LOD\ (\mu g/l) = \frac{(A \times ATT)}{(B \times ATT)} \quad (2\ \mu g/l)$$

where B = peak height (mm) of 2 µg/l quality check standard

A = 5 times the noise level in (mm) at the exact retention time of the trihalomethane or the baseline displacement in (mm) from the theoretical zero at the exact retention time of the trihalomethane.

ATT = Attenuation factor

11. Accuracy and Precision

11.1 One liter of organic-free water was spiked with the trihalomethanes and used to fill septum seal vials which were stored under ambient conditions. The spiked samples were randomly analyzed over a 2-week period of time. The single laboratory data listed in Table II reflect the errors due to the analytical procedure and storage.

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TABLE I

Retention Data for Trihalomethanes

| Trihalomethane | Retention Time Minutes | | |
|---|---|---|---|
| | Column I 1% SP1000 Carbopack B | Acceptable Alternative to Column I 0.4% Carbowax Carbopack C | Column II n-Octane Porasil-C |
| Chloroform | 10.7 | 8.2 | 12.2 |
| Bromodichloromethane | 13.7 | 10.8 | 14.7 |
| Chlorodibromomethane (Dibromochloromethane) | 16.5 | 13.2 | 16.6 |
| Bromoform | 19.2 | 15.7 | 19.2 |

TABLE II

Single Laboratory
Accuracy and Precision for Trihalomethanes

| Spike µg/l | Number Samples | Mean µg/l | Precision Standard Deviation | Accuracy % Recovery |
|---|---|---|---|---|
| **Chloroform** | | | | |
| 1.2 | 12 | 1.2 | 0.14 | 100 |
| 12. | 8 | 11. | 0.16 | 92 |
| 119 | 11 | 105 | 7.9 | 88 |
| **Bromodichloromethane** | | | | |
| 1.6 | 12 | 1.5 | 0.05 | 94 |
| 16. | 8 | 15. | 0.39 | 94 |
| 160 | 11 | 145. | 10.2 | 91 |
| **Chlorodibromomethane** | | | | |
| 2.0 | 12 | 1.9 | 0.09 | 95 |
| 20. | 8 | 19. | 0.70 | 95 |
| 196. | 11 | 185. | 10.6 | 94 |
| **Bromoform** | | | | |
| 2.3 | 12 | 2.3 | 0.16 | 100 |
| 23. | 8 | 23. | 1.38 | 100 |
| 231. | 11 | 223 | 16.3 | 97 |

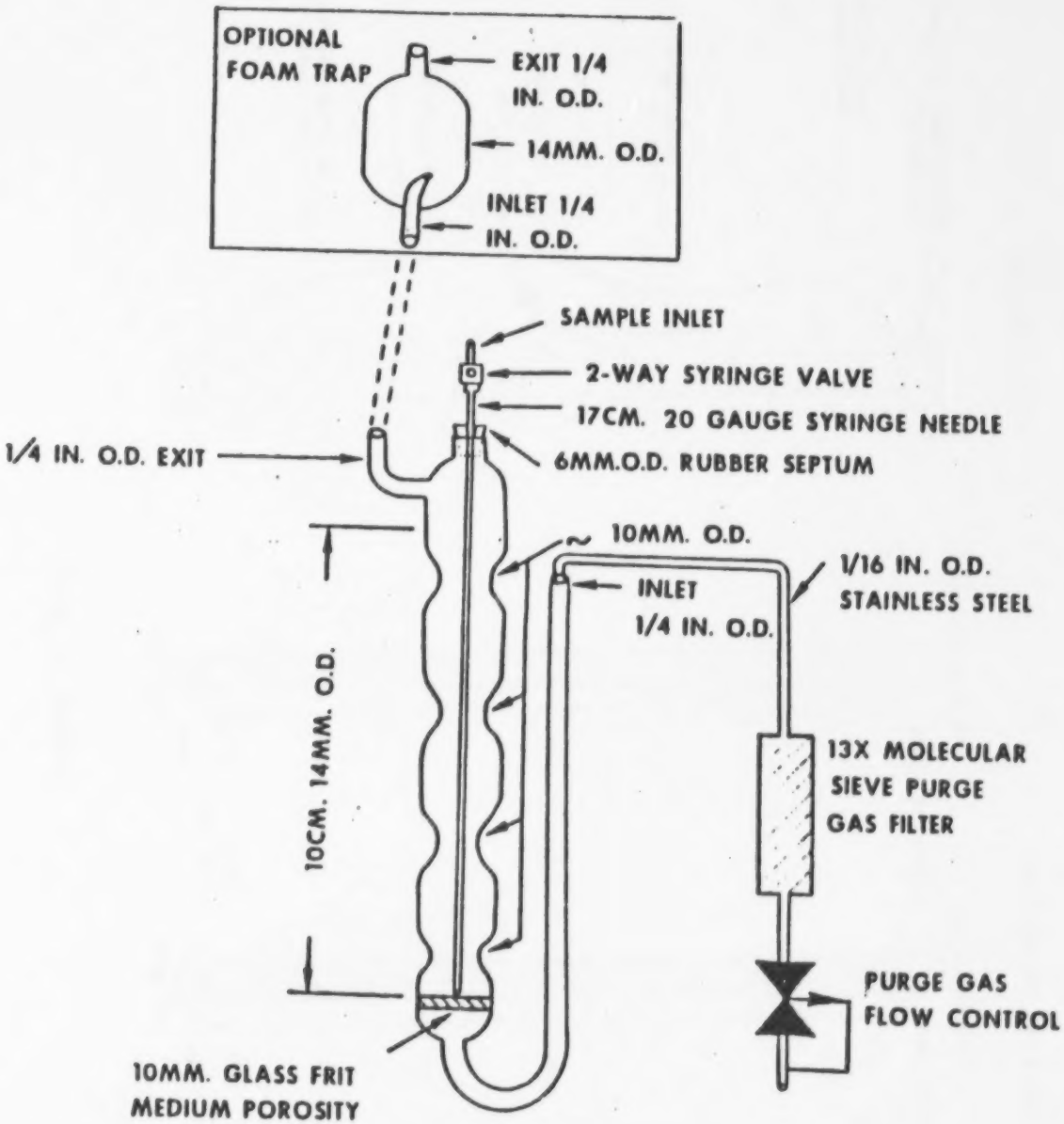


Figure 1. Purging Device

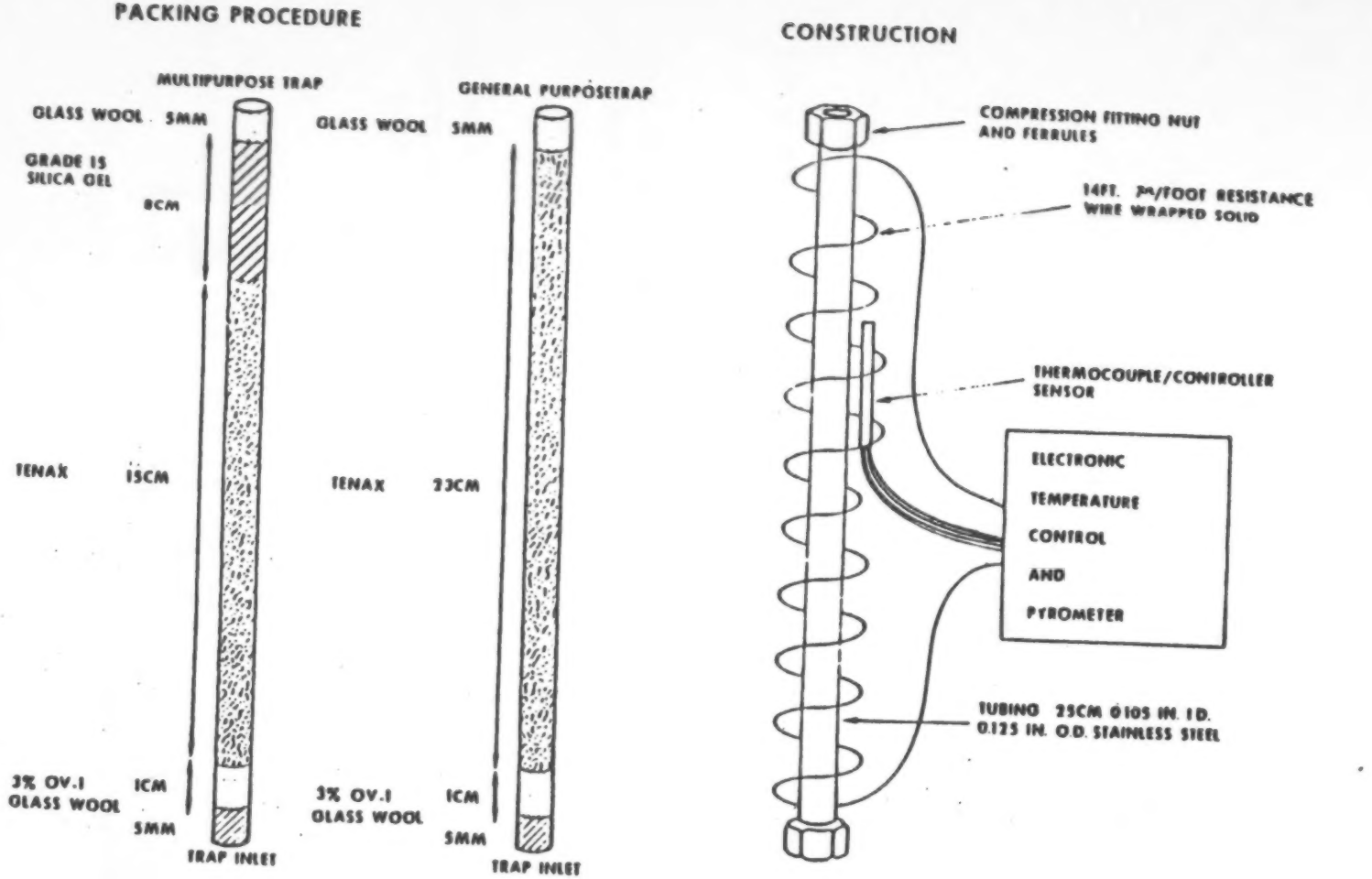


FIGURE 2 TRAP

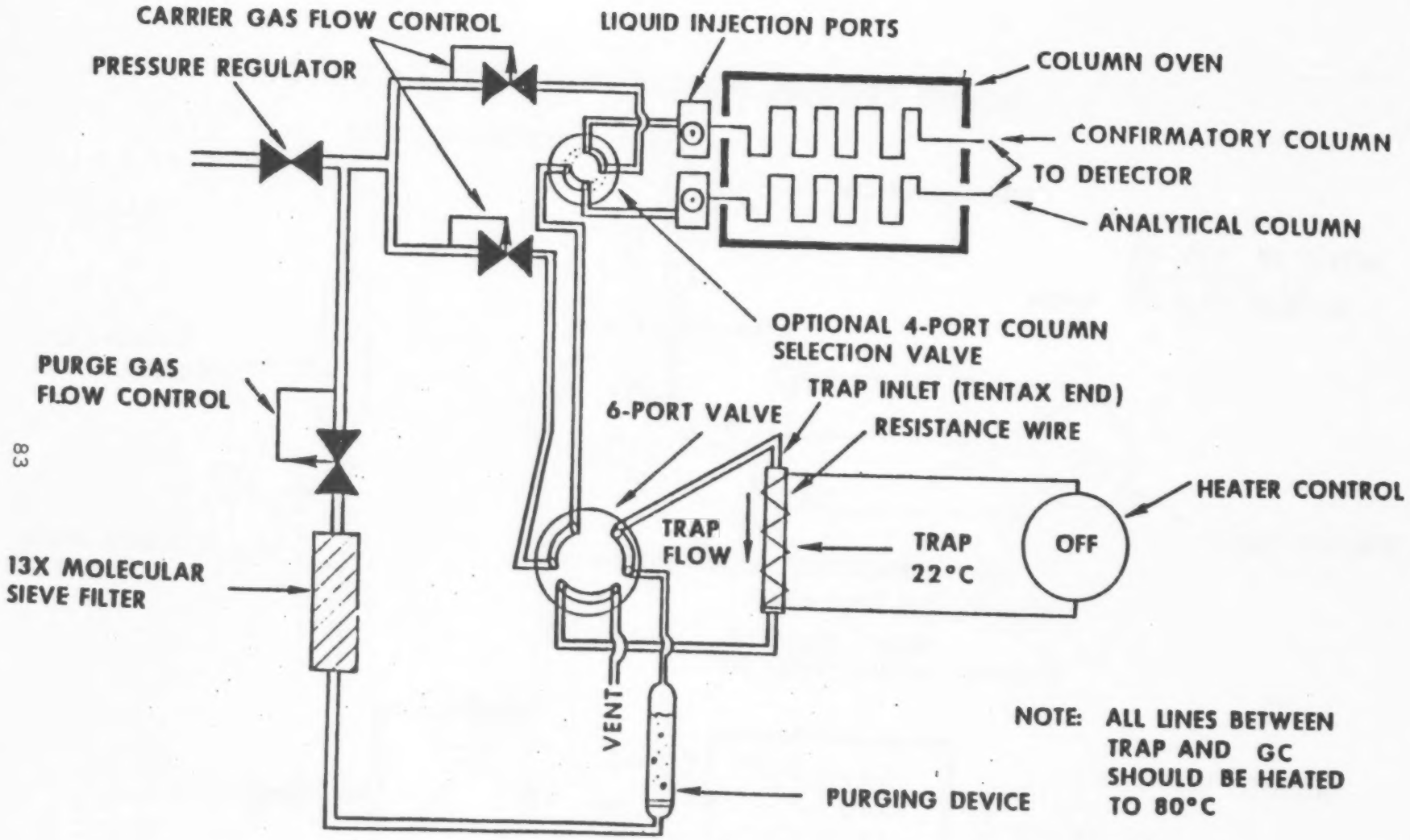


FIGURE 3 PURGE-TRAP SYSTEM (PURGE-SORB MODE)

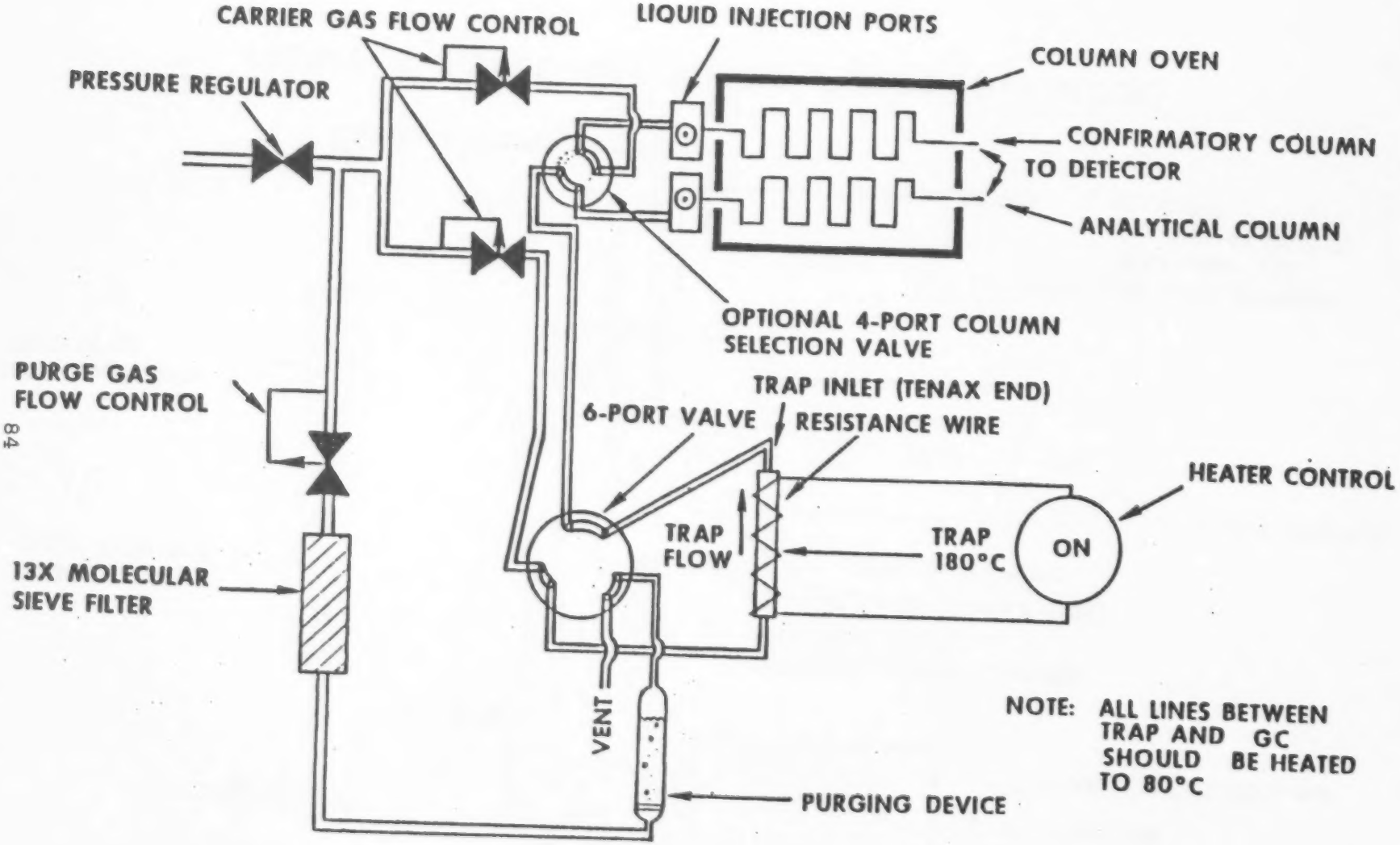


FIGURE 4 PURGE-TRAP SYSTEM (DESORB MODE)

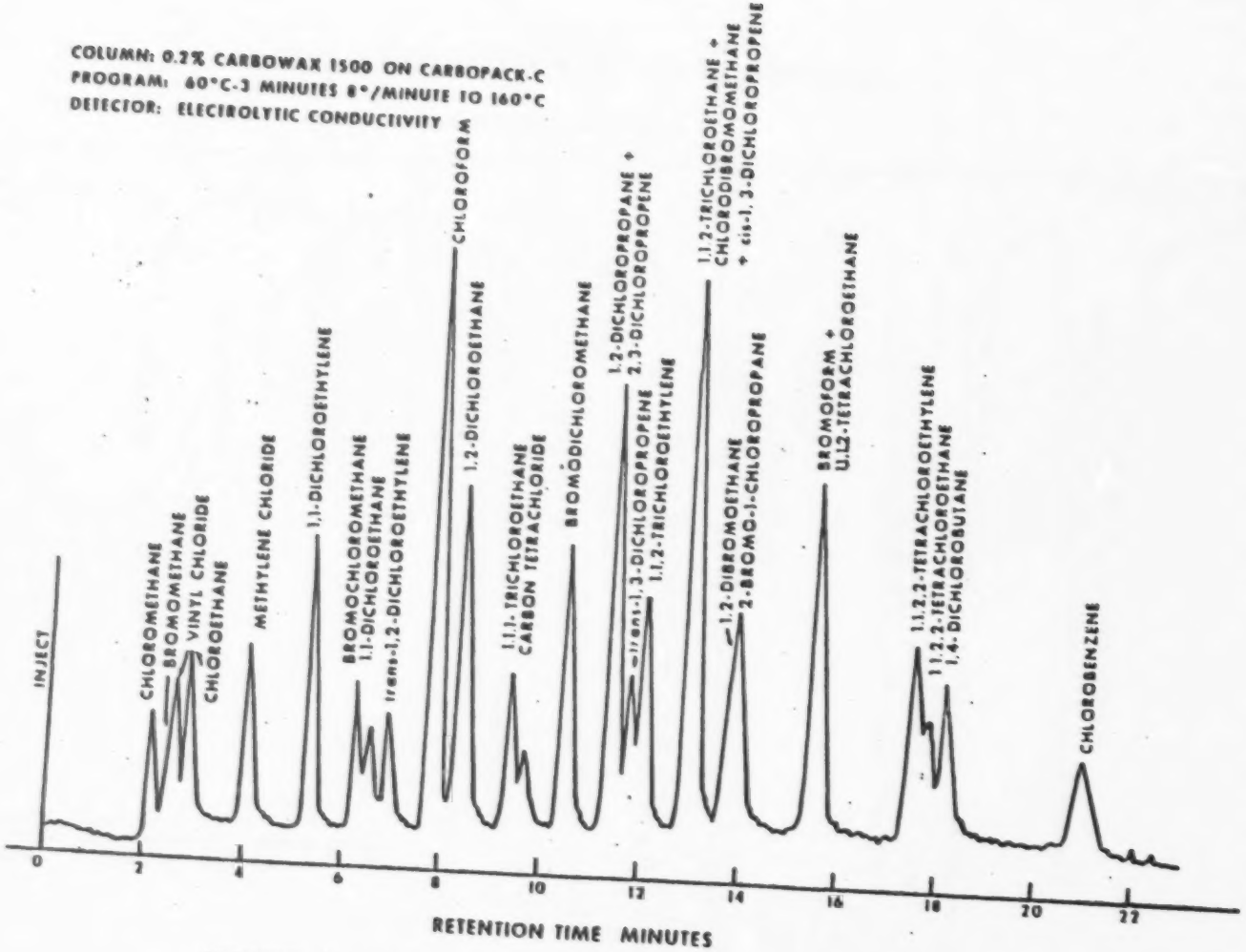


FIGURE 5 CHROMATOGRAM OF ORGANOHALIDES

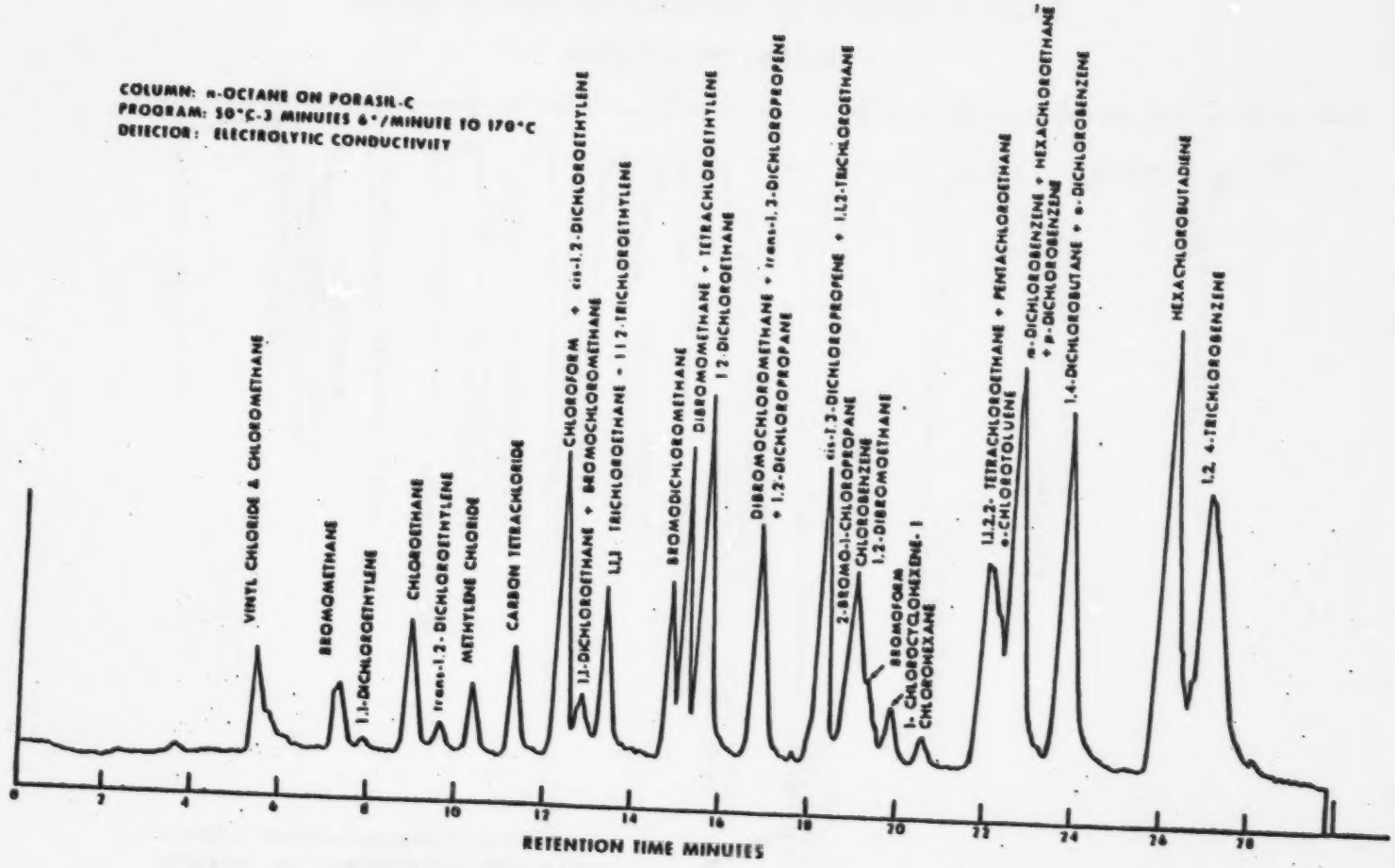


FIGURE 6 CHROMATOGRAM OF ORGANOHALIDES

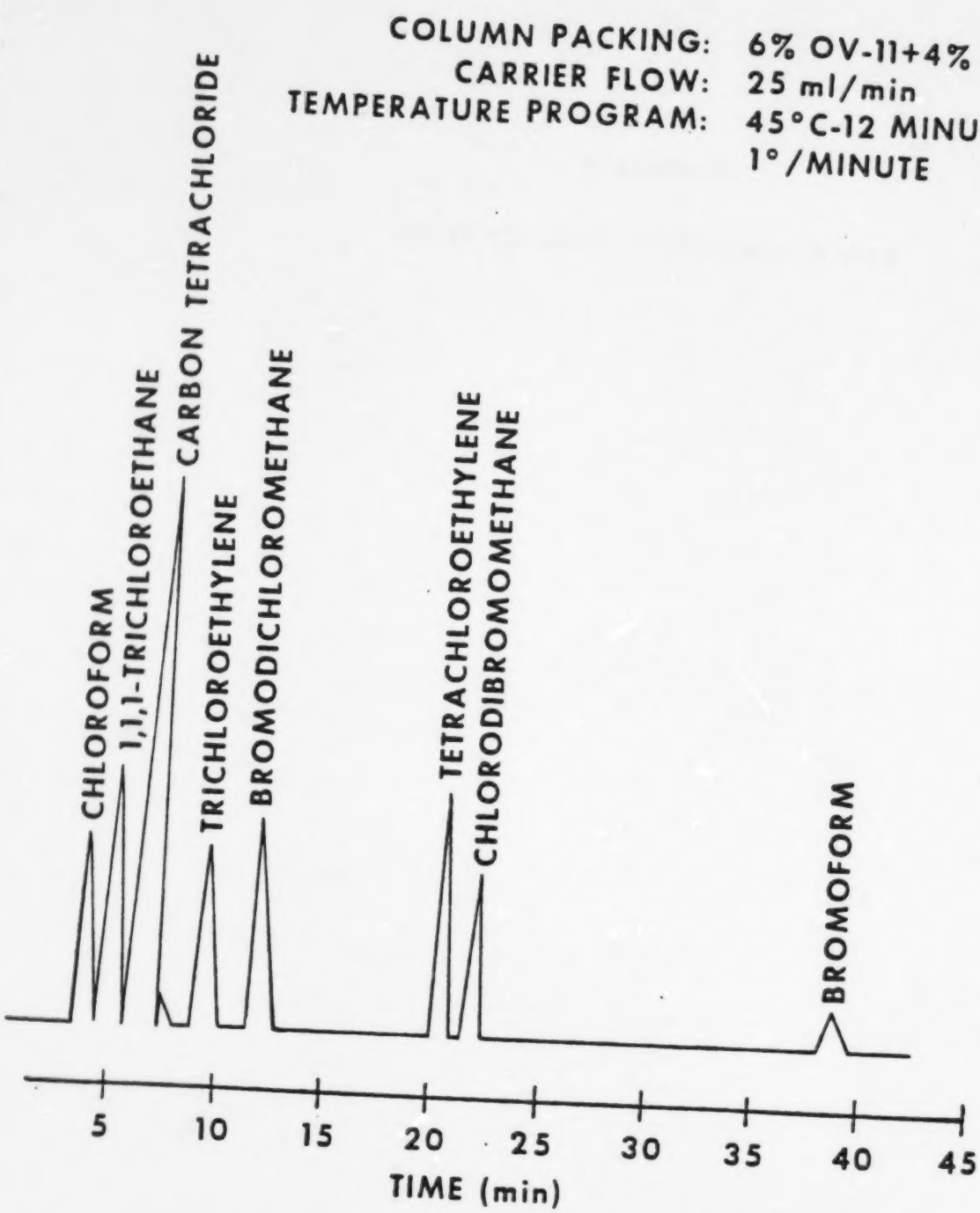


FIGURE 3. EXTRACT OF STANDARD

# APPENDIX B

## SINGLE LABORATORY LINEARITY TESTS

## SINGLE LABORATORY LINEARITY TESTS

Prior to the interlaboratory study, the linearity of Method 501.1 was investigated by the preparation and analysis of aqueous calibration standards of the four trihalomethanes. Analyses were conducted as prescribed by the method. In all cases, 20 µL of methanolic standard was spiked into 100.0 mL of organic-free water in a volumetric flask. The sample was mixed, and 5.0 mL was immediately loaded into a purge-and-trap autosampler. All aqueous standards at a given concentration were analyzed on the same day. The system performance was checked each day using a 20-µg/L aqueous standard. The Tenax GC trap was conditioned at 180°C for 10 minutes each day before samples were introduced. The GC temperature program was initiated while the trap was baking. All instrument parameters are listed in Table B-1.

Retention of trihalomethanes in the autosampler plumbing initially produced carry-over problems in the analysis of successive sets of samples. This problem was eliminated by emptying the purging devices of their samples, loading each with 5.0 mL of organic-free water, and purging each for 10 minutes following the analysis of high-level sample sets (100 µg/L or greater) and for 5 minutes following the analysis of low-level sample sets (<100 µg/L). While it was found to be necessary to follow this procedure between the analyses of each set of samples, it was not required between individual analyses within a set of samples. By setting the desorb and bake times to zero on the liquid sample concentrator, the instrument time required for this purging procedure was only about one hour. This procedure also eliminated the need to wash or bake out the purging devices. A blank was analyzed each day to confirm that significant carry-over was not occurring.

TABLE B-1. INSTRUMENT PARAMETERS FOR EPA METHOD 501.1

Gas Chromatograph: Varian 3700

Column: 1% SP1000 on Carbopack B (60/80 mesh),
2.4 m x 2.5 mm S.S.

GC Temperatures: Injection Port - 220°C
Column - hold at 45°C for 4 min while desorbing trap; increase at 8°C/min to 220°C; hold at 220°C for 1 min
Detector - 220°C

Carrier Gas: Helium at 40 mL/min

Retention Times: Chloroform - 12.0 min
Bromodichloromethane - 14.9 min
Chlorodibromomethane - 17.6 min
Bromoform - 20.2 min

Detector: Hall Model 700 electrolytic conductivity
Furnace Temperature - 1000°C
Flow rate of n-propanol - 0.1 mL/min
Hydrogen flow rate - 80 mL/min

Purge-and-Trap Unit: Tekmar Model LSC-2 with
Model ALS autosampler
Purge - 11 min at <35°C
Desorb - 4 min at 180°C
Bake - 15 min at 180°C
Transfer lines - 140°C
Purge gas - Helium at 40 mL/min
Purge volume - 5 mL
Trap material - Tenax GC

Table B-2 lists the actual concentrations of the aqueous standards. The precision data in Tables B-3 through B-9 include raw area counts obtained in analysis of the standards. The area counts at the various concentration levels can not accurately be related to concentration, because a different attenuation and range was employed for each concentration (see the footnotes for Tables B-3 through B-9. The area counts can, however, be employed to calculate the precision of Method 501.1 at the various concentrations. Included in Tables B-3 through B-9 are calculated values of the mean area count ($\bar{X}$), the number of analyses of each standard (N), the standard deviation of the area counts (S.D.), and the relative standard standard deviation expressed as a percentage [rel. S.D. (%)].

It should be noted that at the 1000-µg/L and 1500-µg/L concentrations, the detector was saturated for chloroform and bromodichloromethane, and at the 1500-µg/L concentration for chlorodibromomethane. Saturation was indicated by the appearance of double peaks and a leveling off of detector response. The data for these three trihalomethanes at these concentrations, therefore, reflect maximal detector output rather than true precision data.

TABLE B-2. CONCENTRATIONS OF TRIHALOMETHANES IN AQUEOUS STANDARDS USED FOR PRECISION DETERMINATIONS (µg/L)

| Nominal concentration | Actual concentrations | | | |
|---|---|---|---|---|
| | Chloroform | Bromodichloro-methane | Chlorodibromo-methane | Bromoform |
| 1 | 0.924 | 0.95 | 1.03 | 1.04 |
| 50 | 52.0 | 53.6 | 58.0 | 58.4 |
| 140 | 130 | 134 | 145 | 146 |
| 250 | 213 | 252 | 242 | 218 |
| 500 | 426 | 504 | 484 | 436 |
| 1,000 | 852 | 1,009 | 968 | 872 |
| 1,500 | 1,476 | 1,424 | 1,781 | 1,300 |

TABLE B-3. METHOD PRECISION AT 1-μg/L CONCENTRATION

| Run number | Area counts x 1000 | | | |
|---|---|---|---|---|
| | Chloroform | Bromodichloro-methane | Chlorodibromo-methane | Bromoform |
| 1 | 284 | 152 | 107 | 39.3 |
| 2 | 347 | 164 | 113 | 52.3 |
| 3 | 253 | 180 | 103 | 49.1 |
| 4 | 297 | 172 | 103 | 42.8 |
| 5 | 325 | 164 | 105 | 51.2 |
| 6 | 375 | 176 | 111 | 47.5 |
| 7 | 347 | 210 | 120 | 50.2 |
| $\bar{X}$ | 318 | 174 | 109 | 47.5 |
| N | 7 | 7 | 7 | 7 |
| S.D. | 42 | 18 | 6 | 4.8 |
| Rel. S.D. (%) | 13 | 11 | 5.7 | 10 |

Range = 10; attenuation = 2.

TABLE B-4. METHOD PRECISION AT 50-µg/L CONCENTRATION

| Run No. | Area counts x 1,000 | | | |
|---|---|---|---|---|
| | Chloroform | Bromodichloromethane | Dibromochloromethane | Bromoform |
| 1 | 1,612 | 1,344 | 1,082 | 685 |
| 2 | 1,542 | 1,395 | 1,063 | 716 |
| 3 | 1,706 | 1,383 | 1,115 | 742 |
| 4 | 1,584 | 1,382 | 1,116 | 663 |
| 5 | 1,771 | 1,519 | 1,210 | 767 |
| 6 | 1,737 | 1,451 | 1,160 | 723 |
| $\bar{X}$ | 1,659 | 1,412 | 1,124 | 716 |
| N | 6 | 6 | 6 | 6 |
| S.D. | 92 | 62 | 54 | 85 |
| Rel. S.D., % | 5.5 | 4.4 | 4.8 | 5.3 |

Range = 100; attenuation = 16.

TABLE B-5. METHOD PRECISION AT 140-µg/L CONCENTRATION

| Run No. | Area counts x 1,000 | | | |
|---|---|---|---|---|
| | Chloroform | Bromodichloromethane | Dibromochloromethane | Bromoform |
| 1 | 5,542 | 4,882 | 4,263 | 2,874 |
| 2 | 5,526 | 4,935 | 4,479 | 3,038 |
| 3 | 5,553 | 5,284 | 4,372 | 2,940 |
| 4 | 5,849 | 5,343 | 4,332 | 2,861 |
| 5 | 6,010 | 5,231 | 4,232 | 2,792 |
| 6 | 6,019 | 5,059 | 4,338 | 2,976 |
| $\bar{X}$ | 5,750 | 5,122 | 4,336 | 2,914 |
| N | 6 | 6 | 6 | 6 |
| S.D. | 237 | 192 | 87 | 89 |
| Rel. S.D., % | 4.1 | 3.7 | 2.0 | 3.0 |

Range = 100; attenuation = 32.

TABLE B-6. METHOD PRECISION AT 250-µg/L CONCENTRATION

| Run No. | Area counts x 1,000 | | | |
|---|---|---|---|---|
| | Chloroform | Bromodichloromethane | Dibromochloromethane | Bromoform |
| 1 | 680 | 753 | 582 | 377 |
| 2 | 738 | 788 | 595 | 385 |
| 3 | 700 | 753 | 575 | 373 |
| 4 | 744 | 802 | 594 | 380 |
| 5 | 718 | 776 | 580 | 372 |
| 6 | 717 | 760 | 581 | 372 |
| 7 | 743 | 792 | 602 | 376 |
| $\bar{X}$ | 720 | 775 | 587 | 376 |
| N | 7 | 7 | 7 | 7 |
| S.D. | 24 | 20 | 9.9 | 4.8 |
| Rel. S.D., % | 3.3 | 2.6 | 1.7 | 1.3 |

Range = 1000; attenuation = 8.

TABLE B-7. METHOD PRECISION AT 500-µg/L CONCENTRATION

| Run No. | Area counts x 1,000 | | | |
|---|---|---|---|---|
| | Chloroform | Bromodichloromethane | Dibromochloromethane | Bromoform |
| 1 | 1,513 | 1,711 | 1,393 | 938 |
| 2 | 1,573 | 1,743 | 1,407 | 961 |
| 3 | 1,698 | 1,865 | 1,474 | 1,002 |
| 4 | 1,712 | 1,855 | 1,479 | 938 |
| 5 | 1,669 | 1,799 | 1,474 | 935 |
| 6 | 1,786 | 1,880 | 1,460 | 1,002 |
| $\bar{X}$ | 1,658 | 1,809 | 1,448 | 996 |
| N | 6 | 6 | 6 | 6 |
| S.D. | 99 | 70 | 38 | 37 |
| Rel. S.D., % | 6.0 | 3.9 | 2.6 | 3.9 |

Range = 1000; attenuation = 16.

TABLE B-8. METHOD PRECISION AT 1,000-µg/L CONCENTRATION

| Run No. | Area counts x 1,000 | | | |
|---|---|---|---|---|
| | Chloroform | Bromodichloromethane | Dibromochloromethane | Bromoform |
| 1 | 2,717 | 2,802 | 2,634 | 1,690 |
| 2 | 2,748 | 2,792 | 2,669 | 1,710 |
| 3 | 2,777 | 2,775 | 2,688 | 1,750 |
| 4 | 2,767 | 2,777 | 2,714 | 1,739 |
| 5 | 2,753 | 2,756 | 2,616 | 1,693 |
| $\bar{X}$ | 2,752 | 2,780 | 2,664 | 1,716 |
| N | 5 | 5 | 5 | 5 |
| S.D. | 23 | 18 | 40 | 27 |
| Rel. S.D., % | 0.8 | 0.6 | 1.5 | 1.6 |

Range = 1000; attenuation = 32.

TABLE B-9. METHOD PRECISION AT 1,500-µg/L CONCENTRATION

| Run No. | Area counts x 1,000 | | | |
|---|---|---|---|---|
| | Chloroform | Bromodichloromethane | Dibromochloromethane | Bromoform |
| 1 | 2,637 | 2,816 | 2,847 | 2,620 |
| 2 | 2,597 | 2,905 | 2,977 | 2,754 |
| 3 | 2,690 | 2,853 | 2,852 | 2,768 |
| 4 | 2,716 | 2,856 | 2,945 | 2,826 |
| 5 | 2,811 | 2,888 | 2,992 | 2,749 |
| $\bar{X}$ | 2,690 | 2,864 | 2,923 | 2,743 |
| N | 5 | 5 | 5 | 5 |
| S.D. | 82 | 34 | 69 | 75 |
| Rel. S.D., % | 3.0 | 1.2 | 2.4 | 2.8 |

Range = 1000; attenuation = 32.

# APPENDIX C

## ANALYSIS OF AMPULS USED IN VALIDATION STUDY OF METHOD 501.1

## ANALYSIS OF AMPULS USED IN VALIDATION STUDY OF METHOD 501.1

Concentrated spiking solutions were prepared and sealed in glass ampuls for the interlaboratory validation study of Method 501.1. The contents of representative ampuls were analyzed, primarily to assure that the more volatile compounds had not been lost during the ampul sealing process. This also would verify that no dilution errors had been made in the preparation of the spiking solutions. Monsanto Research Corporation analyzed the contents of three randomly selected ampuls in triplicate from each concentration for each of the analytes by Method 501.2. The Quality Assurance Branch of EMSL also analyzed the ampuls but used direct injection GC/MS technique. The data in Table C-1 shows close agreement with the true value and the analytical value.

TABLE C-1. VERIFICATION DATA FOR AMPULS USED IN STUDY OF METHOD 501.1 (in parts per billion)

| Ampul number | Chloroform | | Bromo-dichloromethane | | Chloro-dibromomethane | | Bromoform | |
|---|---|---|---|---|---|---|---|---|
| | True value | Analyzed value | True value | Analyzed value | True value | Analyzed value | True value | Analyzed value |
| 1 | 0.86 | 0.82* | 0.88 | 0.87* | 0.84 | 0.82* | 4.84 | 5.15 |
| 2 | 1.14 | 1.1* | 1.16 | 1.14* | 1.15 | 1.13* | 5.93 | 5.51* |
| 3 | 46.0 | 50.8 | 46.0 | 47.6 | 46.0 | 49.2 | 45.8 | 43.0 |
| 4 | 54.1 | 51.4 | 54.4 | 54.2 | 54.3 | 54.4 | 54.0 | 50.4 |
| 5 | 550 | 555* | 550 | 555* | 550 | 526* | 550 | 515* |
| 6 | 450 | 446* | 450 | 450* | 450 | 450* | 450 | 436* |

Note: The asterisk indicates values generated by EPA, while no asterisk indicates values generated by MRC.

# APPENDIX D

## RAW DATA: METHOD 501.1

TABLE D-1. RAW DATA FOR CHLOROFORM ANALYSIS BY WATER TYPE

| YOUDEN PAIR | WATER 1 | | WATER 2 | | WATER 1 | | WATER 2 | | WATER 1 | | WATER 2 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 1 | 2 | 3 | 4 | 3 | 4 | 5 | 6 | 5 | 6 |
| TRUE VALUE UG/L | 0.86 | 1.14 | 0.86 | 1.14 | 46.03 | 54.17 | 46.00 | 54.17 | 550.00 | 650.00 | 550.00 | 650.00 |
| LABORATORY NUMBER | | | | | | | | | | | | |
| 11 | 0.84 | 1.14 | 0.74 | 1.20 | 38.10 | 50.49 | 43.40 | 49.50 | 488.00 | 502.00 | 534.00 | 509.00 |
| 21 | 0.72 | 0.91 | 0.90 | 3.50 | 51.20 | 51.30 | 46.70 | 55.10 | 595.00 | 485.00 | 608.00 | 498.00 |
| 31 | 0.69 | 0.57 | 2.30 | 17.70* | 52.20 | 46.90 | 47.00 | 77.00 | 514.00 | 422.00 | 564.00 | 417.00 |
| 41 | 0.59 | 0.44 | 0.32 | 3.07 | 42.20 | 51.90 | 47.40 | 49.90 | 477.00 | 333.00 | 512.00 | 431.00 |
| 51 | 0.86 | 0.84 | 0.000* | 0.000* | 43.00 | 50.40 | 43.20 | 50.50 | 516.00 | 430.00 | 489.00 | 417.00 |
| 61 | 0.000* | 0.000* | 0.000* | 0.000* | 42.00 | 51.30 | 29.20* | 29.20 | 445.00 | 371.00 | 456.00 | 414.00 |
| 71 | 1.09 | 1.29 | 1.27 | 1.35 | 46.20 | 53.70 | 48.40 | 54.20 | 504.00 | 434.00 | 514.00 | 469.00 |
| 81 | 3.09* | 4.77* | 19.60* | 0.00* | 61.90* | 55.80* | 44.70 | 26.90 | 543.00* | 371.00* | 471.00 | 312.00 |
| 91 | 0.77 | 1.09 | 1.12 | 1.53 | 41.90 | 55.00 | 41.70 | 59.60 | 587.00 | 459.00 | 492.00 | 464.00 |
| 101 | 1.30 | 1.54 | 0.000* | 0.70 | 50.30 | 58.20 | 47.10 | 57.10 | 643.00 | 419.00 | 603.00 | 443.00 |
| 111 | 0.96 | 1.67 | 2.90 | 4.50 | 46.30 | 55.20 | 49.30 | 58.60 | 503.00 | 428.00 | 522.00 | 391.00 |
| 121 | 0.35 | 0.59 | 0.00* | 0.00* | 40.10 | 49.20 | 40.10 | 50.70 | 547.00 | 424.00 | 574.00 | 439.00 |
| 131 | 0.79 | 1.09 | 1.25 | 1.19 | 40.00 | 61.30 | 39.40 | 63.00 | 519.00 | 386.00 | 498.00 | 397.00 |
| 141 | 1.00 | 1.66 | 0.30 | 3.80 | 41.60 | 42.00 | 46.40 | 52.50 | 465.00 | 401.00 | 514.00 | 440.00 |
| 151 | 5.63* | 3.54* | 0.90 | 4.90 | 47.00 | 54.30 | 0.00* | 47.40 | 550.00 | 495.00 | 540.00 | 442.00 |
| 161 | 0.49 | 0.79 | 0.00* | 0.00* | 47.00 | 50.60 | 44.20 | 55.60 | 159.00 | 157.00 | 139.00* | 145.00* |
| 171 | 1.70 | 1.79 | 1.70 | 1.75 | 55.00 | 79.00* | 55.00 | 72.00 | 136.00 | 203.00 | 629.00 | 620.00 |
| 181 | 0.25 | 0.87 | 0.00* | 0.00* | 42.00 | 52.80 | 49.20* | 76.90 | 482.00 | 460.00 | 719.00 | 657.00 |
| 191 | 1.03 | 1.59 | 0.21* | 1.06* | 5.77* | 6.00* | 4.62* | 5.10* | 46.20 | 40.40* | 42.90* | 42.30* |
| 201 | 0.85 | 0.59 | 2.55* | 5.90* | 132.00* | 160.00* | 36.10* | 90.10* | 859.00 | 549.00 | 1490.00* | 1200.00* |

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER

TABLE D-2. RAW DATA FOR BROMODICHLOROMETHANE ANALYSIS BY WATER TYPE

| YOUDEN PAIR | WATER 1 | | WATER 2 | | WATER 1 | | WATER 2 | | WATER 1 | | WATER 2 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 1 | 2 | 3 | 4 | 3 | 4 | 5 | 6 | 5 | 6 |
| TRUE VALUE UG/L | 0.88 | 1.14 | 0.99 | 1.15 | 46.00 | 54.43 | 46.00 | 54.43 | 550.00 | 650.00 | 550.00 | 650.00 |
| LABORATORY NUMBER | | | | | | | | | | | | |
| 11 | 1.02 | 1.22 | 0.83 | 1.01 | 37.00 | 49.10 | 40.90 | 46.90 | 498.00 | 490.00 | 522.00 | 479.00 |
| 21 | 0.64 | 0.84 | 0.91 | 0.84 | 46.90 | 51.60 | 44.50 | 59.10 | 595.00 | 481.00 | 412.00 | 474.00 |
| 31 | 0.33 | 0.64 | 1.49 | 2.01 | 57.00 | 47.90 | 41.00 | 50.10 | 513.00 | 428.00 | 542.00 | 391.00 |
| 41 | 0.66 | 0.94 | 1.97* | 5.51* | 34.60 | 42.70 | 41.70 | 44.50 | 384.00 | 267.00 | 479.00 | 377.00 |
| 51 | 0.83 | 1.01 | 0.70 | 0.03* | 45.90 | 53.70 | 43.70 | 50.90 | 549.00 | 458.00 | 526.00 | 444.00 |
| 61 | 0.00* | 0.00* | 0.00* | 0.00* | 45.00 | 55.30 | 55.60 | 51.30 | 44.00 | 330.00 | 474.00 | 373.00 |
| 71 | 0.71 | 1.14 | 2.40 | 2.63 | 44.20 | 45.50 | 47.70 | 52.40 | 516.00 | 449.00 | 531.00 | 453.00 |
| 81 | 1.44 | 3.39* | 5.50* | 0.00* | 54.20 | 52.50 | 44.10 | 42.10 | 549.00 | 549.00 | 417.00 | 305.00 |
| 91 | 1.17 | 1.40 | 0.91 | 1.17 | 42.00 | 55.40 | 50.20 | 70.50 | 551.00 | 427.00 | 558.00 | 449.00 |
| 101 | 0.86 | 1.22 | 0.97 | 1.34 | 45.00 | 54.40 | 40.10 | 69.00 | 594.00 | 421.00 | 706.00 | 464.00 |
| 111 | 1.75 | 2.67* | 1.00 | 2.60 | 47.00 | 50.90 | 49.40 | 59.20 | 507.00 | 425.00 | 495.00 | 385.00 |
| 121 | 0.71 | 0.84 | 0.24 | 0.60 | 60.20 | 76.20* | 49.10 | 79.30 | 961.00 | 739.00 | 950.00 | 774.00 |
| 131 | 0.60 | 1.09 | 1.00 | 0.89 | 42.40 | 64.80 | 41.10 | 49.80 | 113.00 | 513.00 | 99.50 | 592.00 |
| 141 | 0.42 | 0.49 | 1.90 | 2.93 | 38.80 | 45.50 | 41.80 | 52.20 | 492.00 | 409.00 | 524.00 | 476.00 |
| 151 | 0.41 | 0.59 | 0.84 | 1.35 | 43.60 | 53.20 | 14.40* | 52.40 | 553.00 | 456.00 | 537.00 | 449.00 |
| 161 | 0.38 | 0.49 | 0.10 | 0.00* | 48.30 | 48.10 | 44.10 | 55.00 | 228.00 | 214.00 | 234.00 | 207.00 |
| 171 | 1.40 | 1.49 | 1.49 | 1.45 | 54.00 | 63.00 | 54.30 | 63.00 | 162.00 | 211.00 | 720.00 | 649.00 |
| 181 | 0.84 | 0.91 | 0.00* | 0.00* | 44.00 | 58.10 | 49.40 | 55.40 | 530.00 | 458.00 | 620.00 | 494.00 |
| 191 | 0.00* | 0.00* | 0.00* | 0.00* | 4.61* | 5.01* | 4.40* | 5.46* | 49.90* | 49.70* | 58.55* | 47.13* |
| 201 | 0.00* | 0.30* | 1.04* | 1.50* | 89.20* | 104.00* | 99.90* | 99.33* | 1300.00* | 1100.00* | 1990.00* | 1230.00* |

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER

TABLE D-3. RAW DATA FOR CHLORODIBROMOMETHANE ANALYSIS BY WATER TYPE

| YOUDEN PAIR | WATER 1 | | WATER 2 | | WATER 1 | | WATER 2 | | WATER 1 | | WATER 2 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TRUE VALUE UG/L | 1<br>0.84 | 2<br>1.19 | 1<br>0.84 | 2<br>1.19 | 3<br>48.60 | 4<br>54.37 | 3<br>44.09 | 4<br>54.13 | 5<br>550.00 | 6<br>450.00 | 5<br>550.00 | 6<br>450.00 |
| LABORATORY NUMBER | | | | | | | | | | | | |
| 11 | 0.56 | 0.99 | 0.89 | 1.01 | 38.90 | 49.69 | 37.79 | 47.40 | 537.00 | 514.00 | 511.00 | 479.00 |
| 21 | 0.49 | 0.79 | 0.54 | 0.89 | 45.30 | 53.30 | 49.80 | 57.90 | 591.00 | 478.00 | 579.00 | 473.00 |
| 31 | 0.13 | 0.69 | 0.91 | 1.29 | 73.10* | 55.09 | 55.19 | 59.49 | 604.00 | 487.00 | 530.00 | 499.00 |
| 41 | 1.48 | 2.51 | 3.17* | 4.13* | 49.40 | 62.79 | 57.09 | 64.70 | 579.00 | 417.00 | 493.00 | 545.00 |
| 51 | 0.62 | 0.89 | 0.49 | 1.79 | 49.20 | 55.09 | 41.69 | 55.50 | 549.00 | 442.00 | 542.00 | 499.00 |
| 61 | 0.00* | 0.00* | 0.00* | 0.00* | 46.90 | 65.50 | 38.89 | 65.90 | 734.00 | 565.00 | 598.00 | 492.00 |
| 71 | 0.59 | 0.94 | 4.30* | 5.03* | 46.60 | 57.49 | 54.50 | 60.10 | 529.00 | 460.00 | 534.00 | 442.00 |
| 81 | 1.76 | 2.23 | 2.34* | 0.99 | 42.80 | 48.69 | 41.69 | 44.30 | 498.00 | 498.00 | 393.00 | 319.00 |
| 91 | 1.29 | 1.89 | 0.00* | 0.00* | 41.30 | 54.40 | 55.40 | 69.70 | 574.00 | 447.00 | 574.00 | 479.00 |
| 101 | 0.69 | 1.01 | 0.44 | 0.81 | 46.20 | 58.39 | 58.40 | 66.60 | 568.00 | 493.00 | 799.00 | 516.00 |
| 111 | 3.74* | 3.10 | 0.00* | 0.00* | 55.10 | 62.40 | 55.90 | 64.20 | 681.00 | 620.00 | 691.00 | 594.00 |
| 121 | 0.69 | 0.37 | 2.39 | 0.69 | 32.30 | 42.00 | 33.40 | 44.70 | 760.00 | 603.00 | 764.00 | 632.00 |
| 131 | 0.59 | 1.19 | 0.90 | 0.90 | 41.40 | 66.80 | 39.90 | 61.90 | 113.00 | 544.00 | 92.10 | 622.00 |
| 141 | 0.27 | 0.29 | 0.47 | 0.56 | 34.60 | 41.09 | 37.93 | 44.20 | 492.00 | 631.00 | 532.00 | 476.00 |
| 151 | 0.34 | 0.59 | 0.91 | 0.79 | 40.70 | 50.70 | 16.10 | 48.40 | 536.00 | 439.00 | 511.00 | 472.00 |
| 161 | 0.13 | 0.21 | 1.41 | 0.79 | 48.70 | 45.90 | 52.90 | 61.10 | 308.00 | 290.00 | 391.00 | 277.00 |
| 171 | 1.00 | 1.39 | 1.00 | 1.19 | 49.80 | 32.20 | 49.80 | 32.20 | 141.00 | 165.00 | 694.00 | 539.00 |
| 181 | 0.88 | 0.94 | 0.49 | 0.42 | 39.10 | 47.59 | 37.60 | 46.60 | 452.00 | 385.00 | 446.00 | 386.00 |
| 191 | 0.00* | 0.00* | 0.00* | 0.00* | 3.64* | 4.09* | 3.71* | 4.55* | 45.00* | 43.59* | 55.49* | 42.49* |
| 201 | 0.00* | 0.07* | 0.00* | 0.00* | 55.20 | 72.90 | 76.90 | 68.00 | 1000.00 | 800.00 | 1040.00 | 827.00 |

* = REJECTED

WATER LEGEND

1 = DISTILLED WATER
2 = TAP WATER

TABLE D-4. RAW DATA FOR BROMOFORM ANALYSIS BY WATER TYPE

| | WATER 1 | | WATER 2 | | WATER 1 | | WATER 2 | | WATER 1 | | WATER 2 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| WIDEN PAIR | 1 | 2 | 1 | 2 | 3 | 4 | 3 | 4 | 5 | 6 | 5 | 6 |
| TRUE VALUE UG/L | 4.84 | 5.91 | 4.44 | 5.31 | 49.80 | 54.39 | 49.90 | 54.31 | 550.00 | 650.00 | 550.00 | 650.00 |
| LABORATORY NUMBER | | | | | | | | | | | | |
| 11 | 3.11 | 3.82 | 2.80 | 3.51 | 37.10 | 61.40 | 44.90 | 57.40 | 549.00 | 514.00 | 541.00 | 479.00 |
| 21 | 3.04 | 4.09 | 3.69 | 4.17 | 49.00 | 51.90 | 49.90 | 54.90 | 582.00 | 486.00 | 575.00 | 474.00 |
| 31 | 3.37 | 3.94 | 4.17 | 4.09 | 84.90 | 58.50 | 99.90 | 63.50 | 664.00 | 501.00 | 499.00 | 542.00 |
| 41 | 4.01 | 5.52 | 3.96 | 3.69 | 38.70 | 49.39 | 44.40 | 52.10 | 482.00 | 354.00 | 538.00 | 441.00 |
| 51 | 3.32 | 4.21 | 2.44 | 4.11 | 43.40 | 49.20 | 94.40 | 49.10 | 917.00 | 403.00 | 569.00 | 413.00 |
| 61 | 0.00* | 0.00* | 0.00* | 0.00* | 66.10 | 62.90 | 18.99 | 72.20 | 968.00 | 687.00 | 1124.00 | 812.00 |
| 71 | 3.90 | 5.20 | 4.50 | 8.70 | 43.50 | 50.80 | 99.30 | 59.49 | 604.00 | 454.00 | 543.00 | 424.00 |
| 81 | 5.39 | 5.09 | 4.22 | 5.39 | 38.10 | 41.70 | 39.40 | 41.00 | 506.00 | 504.00 | 344.00 | 261.00 |
| 91 | 5.35 | 7.35 | 1.99 | 7.21 | 41.60 | 57.00 | 44.80 | 59.10 | 563.00 | 435.00 | 564.00 | 453.00 |
| 101 | 6.98 | 7.99 | 4.79 | 8.35 | 52.20 | 58.30 | 93.40 | 63.60 | 475.00 | 411.00 | 687.00 | 422.00 |
| 111 | 0.95 | 13.30* | 1.09 | 0.00* | 59.40 | 53.30 | 99.90 | 62.10 | 487.00 | 473.00 | 464.00 | 469.00 |
| 121 | 0.00* | 6.59 | 0.30* | 0.00* | 6.99 | 8.89* | 4.20 | 10.03* | 739.00 | 567.00 | 733.00 | 557.00 |
| 131 | 5.24 | 5.67 | 6.19 | 5.47 | 43.60 | 56.40 | 49.20 | 33.40 | 74.00 | 547.00 | 41.00 | 473.00 |
| 141 | 1.26 | 1.94 | 1.49 | 1.45 | 31.10 | 35.80 | 29.40 | 37.50 | 519.00 | 454.00 | 565.00 | 498.00 |
| 151 | 3.10 | 3.93 | 3.24 | 4.21 | 45.40 | 58.40 | 17.40 | 53.40 | 628.00 | 510.00 | 574.00 | 478.00 |
| 161 | 0.73 | 1.83 | 1.47 | 2.51 | 39.70 | 40.20 | 38.10 | 59.40 | 442.00 | 427.00 | 439.00 | 410.00 |
| 171 | 2.70 | 4.10 | 2.70 | 4.17 | 54.50 | 50.20 | 94.50 | 50.23 | 124.00 | 201.00 | 1150.00 | 980.00 |
| 181 | 4.10 | 2.99 | 3.99 | 6.04 | 44.00 | 59.00 | 47.10 | 94.00 | 534.00 | 493.00 | 549.00 | 474.00 |
| 191 | 0.00* | 0.00* | 0.00* | 0.00* | 0.00* | 0.00* | 0.00* | 0.00* | 55.70* | 51.80* | 50.40* | 43.37* |
| 201 | 0.00* | 0.00* | 0.00* | 0.00* | 49.60 | 65.20 | 76.40 | 55.00 | 1000.00 | 790.00 | 944.00 | 754.00 |

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER

TABLE D-5. BLANK VALUES FOR VALIDATION ANALYSES

| Laboratory | Distilled water | | | | Tap water | | | |
|---|---|---|---|---|---|---|---|---|
| | Chloroform | Bromodichloromethane | Chlorodibromomethane | Bromoform | Chloroform | Bromodichloromethane | Chlorodibromomethane | Bromoform |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0 | 0 | 0 | 0 | 34.5 | 4.82 | 0.73 | 0 |
| 3 | <0.02 | <0.02 | <0.02 | <0.02 | 62.0 | 1.00 | <0.02 | <0.08 |
| 4 | 8.90 | 4.52 | .77 | 0 | 17.3 | 4.29 | 1.49 | 0 |
| 5 | 0.03 | 0 | 0 | 0.21 | 18.1 | 12.7 | 6.10 | 0.24 |
| 6 | 0 | 0 | 0 | 0 | (55.0)[a] | (16.8) | (7.40) | (0.34) |
| 7 | <0.2 | <0.2 | <0.2 | <0.5 | 39.1 | 4.23 | 0 | 0 |
| 8 | 0.79 | 0 | 0 | 0 | 1.0 | 4.4 | 6.1 | 12.9 |
| 9 | 0 | 0 | 0 | 0 | 52.6 | 13.9 | 3.22 | 0 |
| 10 | 0 | 0 | 0 | 0 | 81.3 | 32.0 | 10.6 | 1.89 |
| 11 | 0 | 0 | 0 | 0 | (74.1, 71.6)[b] | (31.5, 33.7) | (9.30, 12.4) | (1.70, 2.4) |
| 12 | 0.96 | 0 | 0 | 0 | 68.9 | 7.66 | 0.14 | 0 |
| 13 | 0 | 0 | 0 | 0 | 12.3 | 14.6 | 17.5 | 7.28 |
| 14 | 0.37 | 0.09 | 0.15 | 0.22 | 34.7 | 9.54 | 0.37 | 0 |
| 15 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 16 | 0.10 | 0.05 | 0.18 | 0.09 | 15.5 | 5.83 | 1.42 | 0.11 |
| 17 | 0 | 0 | 0 | 0 | 34.6 | 2.42 | 0 | 0 |
| 18 | 0.45 | 0.22 | 0 | 0 | 12.0 | 14.5 | 8.12 | 0.35 |
| 19 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 20 | 1.24 | <0.5 | <0.5 | <0.5 | 27.1 | 4.50 | 0.45 | 0 |
| | | | | | 0.64 | 0 | 0 | 0 |
| | | | | | 7.90 | 0.70 | <0.5 | <0.5 |

[a]Values in parentheses for ampuls 5 and 6.

[b]First value in paranthesis for ampuls 3 and 4, second value in parenthesis for ampuls 5 and 6.